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An analysis of chemical reactor stability and control—I

The possibility of local control, with perfect or imperfect control mechanisms

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Abstract—To design rationally a chemical reactor with its associated control equipment, it is necessary to study the transient behaviour of the system. In this series of papers a well-agitated continuous reactor either of the liquid or fluidized variety is considered under various types of control and criteria are derived enabling one to determine under what conditions different modes of control are successful. This first part, after an introduction to the whole subject, introduces the method of linear approximation and goes on to discuss the possibility of controlling a naturally unstable steady state by various systems of perfect and imperfect control.

Résumé—L'étude rationnelle d'un réacteur chimique avec son appareillage de contrôle, nécessite la connaissance du comportement transitoire du système. Dans cette série d'articles, les auteurs considèrent avec différents types de contrôle, un réacteur continu bien agité, soit à liquide, fluide ou variétés fluidisées. On obtient ainsi des critères permettant de déterminer dans quelles conditions ces divers modes de contrôle conviennent le mieux. Après une introduction relative à l'ensemble du sujet, cette première partie présente une méthode d'approximation linéaire, et se poursuit par la discussion de la possibilité de contrôler un état de régime instable naturellement, par divers systèmes de contrôle.

Zusammenfassung—Zur rationellen Berechnung eines chemischen Reaktors und der zugehörigen Regeleinrichtung ist es notwendig, das nicht-stationäre Verhalten des Systems zu untersuchen. In dieser Reihe von Veröffentlichungen soll ein gut gerührter kontinuierlicher Reaktor mit flüssiger Phase oder als Fliessbett unter verschiedenen Regelungsarten betrachtet werden. Dabei will man die Kriterien kennenlernen, nach denen es sich entscheiden lässt, unter welchen Bedingungen die verschiedenen Regelungsarten erfolgreich arbeiten. Dieser erste Teil gibt, nach einer Einführung in den gesamten Gegenstand, einen Überblick über die Methode der linearen Approximation und diskutiert dann die Möglichkeit, einen von Natur aus unstabilen stationären Zustand durch verschiedene Systeme volständiger und unvollständiger Regelung zu regeln.

1. INTRODUCTION

THE behaviour of the continuous flow stirred tank reactor has received considerable attention since it was first discussed by MACMULLIN and WEBER [9] and more particularly since DENBIGH's paper in 1944 [5]. VAN HEERDEN [12] showed how certain steady states are possible at which the reactor behaves autothermically and that not all of these are stable. The first treatment of the transient behaviour, taking into account the essential non-linearity of the problem, was given in 1955, [1] and [2]. The methods of non-linear mechanics, which have been developed over the past 50 years, were used to study the approach to the steady states and their stability. It is the purpose here to use these methods to study the

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problem of controlling such a reactor at a steady state. They prove admirably suited to the discussion of this problem and some care is taken to present them in a manner appealing to the chemical engineer.

The two principal notions involved are those of the locally linearized equations (par. 3) and the phase plane (par. 8). The former is a set of linear equations which approximate to the non-linear ones in the immediate vicinity of a steady state and allow the question of its stability to be determined. The latter is the representation of the behaviour of the reactor as a curve in a plane with co-ordinates temperature and composition and this shows if and how the steady state is approached from given initial conditions. The former notion is used in par. 5 to decide what form of control will be successful and in par. 9 to show the nature of the steady states during the evolution of a successful control. The latter, together with certain topological arguments based on it, is used in par. 9 to show the complex nature of the control problem and to predict the phase plane configuration. In par. 10 another tool of non-linear mechanics is introduced, the so-called bifurcation theory of POINCARE [11] to discuss the interesting phenomenon of limited control which may arise even when the controlled steady state is stable. These methods are exemplified and confirmed by an extensive series of calculations described in par. 11. Further topics necessary to tie in the loose ends of this discussion are presented in the remaining paragraphs: p. 5 imperfect control, such as arises by the time lags in an actual servo-mechanism; par. 13, off–on control, the limit at very high amplifications when an instrument meets the limits of its movement almost instantaneously; par. 14, the extension of the discussion to many reactions taking place simultaneously in a series of reactors.

2. THE EQUATIONS

The main concern will be with a single continuous agitated tank reactor. This is a vessel of volume V into which a stream of reactants flows at a constant flow rate q. The vessel is stirred so that the composition and temperature of its contents are constant throughout and these are the composition and temperature of the product stream. For the moment attention will be confined to a single reaction taking place between n chemical species and involving no change of volume. Such a reaction may be written

$$\sum_{j=1}^{n-1} A_j X_j - X = 0 \qquad (2.1)$$

where one of the reactants to be designated by X without a subscript has been singled out. This choice is arbitrary, but if it is chosen to be that reactant which would be first exhausted if the reaction were not limited by equilibrium then the concentration x of this substance cannot be greater than its influent concentration x_0. Let x_j and x_{j0} be the concentrations (in moles per unit volume) and influent concentrations of the species X_j, T be the temperature of the reactor and t the time. Then a unique reaction rate R can be defined, which will in general be a function of all concentrations and the temperature, by

$$\frac{1}{A_j}\left(\frac{dx_j}{dt}\right)_r = -\left(\frac{dx}{dt}\right)_r = R\,(x_j, x, T)$$

where $\left(\frac{d}{dt}\right)_r$ denotes the rate of change of concentration due to reaction only. This reaction rate is unique for by the stoicheiometry of the reaction

$$x_{j0} - x_j = -A_j\,(x_0 - x) \quad (j = 1, 2, \ldots n-1) \qquad (2.2)$$

i.e.
$$\frac{1}{A_j}\frac{dx_j}{dt} = -\frac{dx}{dt}$$

so that R can be uniquely defined as a reaction rate in moles per unit volume per unit time.

A mass balance for each substance gives the equations

$$V\frac{dx}{dt} = q\,(x_0 - x) - VR \qquad (2.3)$$

$$V\frac{dx_i}{dt} = q\,(x_{i0} - x_i) + V\,A_i\,R \qquad (2.3a)$$

but, by substituting from (2.2) in (2.3a), (2.3) is obtained so that this is the only equation needed. Moreover one can substitute in $R\,(x_j, x, T)$ the expressions for x_i given by (2.2) and have

$R \equiv R(x, T; x_0, x_{j0}) = R(x, t)$ in which x_0 and x_{i0} appear only as parameters.

Let $(-\Delta H)$ = heat evolved per mole of X formed
c = specific heat of reacting mixture
ρ = density of reacting mixture
T = temperature of reacting mixture
T_0 = inlet temperature of reactants
U^* = heat per unit volume removed from the reactor by the cooling system. U^* is a function of T and the temperature and flow rate of the coolant.

Then a heat balance for the reactor gives

$$Vc\rho \frac{dT}{dt} = qc\rho (T_0 - T) - VU^* - (-\Delta H) VR \quad (2.4)$$

To avoid undue complication it is assumed that the thermal properties and inlet composition of the reactants are sensibly constant. This is no essential restriction and it could be removed at any time, but it does save carrying along a number of rather slowly varying functions of temperature.

A natural unit of time is V/q the so-called holding time of the reactor; similarly x_0 is a useful unit of concentration and if X is chosen as suggested above (x/x_0) never exceeds unity; the natural unit for temperature is the difference in temperature, $-\Delta H x_0/c\rho$, which would result from the complete conversion of X. Thus the following substitutions

$\tau = qt/V$ = reduced time
$\xi = x/x_0$ = reduced concentration
$\eta = c\rho T/(-\Delta H) x_0$ = reduced temperature
$P = VR/qx_0$ = reduced reaction rate
$U = VU^*/qx_0(-\Delta H)$ = reduced heat removal

reduce the mass and energy balance to

$$\dot{\xi} = \frac{d\xi}{d\tau} = 1 - \xi - P(\xi, \eta) \quad (2.5)$$

$$\dot{\eta} = \frac{d\eta}{d\tau} = (\eta_0 - \eta) - P(\xi, \eta) - U(\eta) \quad (2.6)$$

The steady state values ξ_s and η_s of the concentration and temperature are such as to make $\dot{\xi}$ and $\dot{\eta}$ vanish simultaneously. These may be found by first of all solving $\dot{\xi} = 0$ for ξ as a function of η, say $\eta = \xi_s(\eta)$, and then substituting in the equation $\eta = 0$. Re-arranging, there results

$$\eta - \eta_0 + U(\eta) = -P(\xi_s(\eta), \eta) \quad (2.7)$$

This equation may be given a physical interpretation as is done by Van Heerden [12]. For writing it in the original variables

$$qc\rho (T - T_0) + VU^* = -(-\Delta H) VR$$

the left hand side is the total rate of heat removal both in warming up the reactants and by the cooling system. The right hand side gives the rate of heat generation and for a steady state the two must be equal. In general, the left hand side of equation (2.7) does not depart much from a linear function of η such as is shown by the line L in Fig. 1. The right hand side is generally sigmoid in shape (cf. the curve R in Fig. 1) though it has been shown [2] that more complex shapes are possible. Thus in cases commonly encountered there are three steady states corresponding to the intersections A, B, C of L and R in Fig. 1.

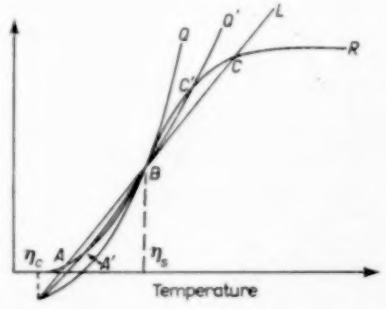

Fig. 1. Steady states with and without control.

The steady state corresponding to the point B in Fig. 1 is clearly unstable, for, for slightly higher temperatures the heat generated is greater than the heat absorbed and temperature would continue to rise until the steady state C were reached. Similarly a slight decrease of temperature would send the system to the steady state A. It is evidently necessary for stability that the

gradient of L should be greater than that of R at the point of intersection.

From (2.5)

$$(1 + P_\xi)\frac{d\xi_s}{d\eta} + P_\eta = 0$$

(the notation $P_\xi = \frac{\partial P}{\partial \xi}$ is being used) so that

$$-\frac{d}{d\eta}P(\xi_s, \eta) = -P_\xi\frac{d\xi_s}{d\eta} - P_\eta = -P_\eta/(1 + P_\xi).$$

It is therefore necessary for stability that

$$(1 + P_\xi)(1 + U_\eta) > -P_\eta \qquad (2.8)$$

It will be shown in the next paragraph that this condition is not sufficient, it is further necessary for stability that $2 + P_\xi + U_\eta > -P_\eta$ but this latter condition does not seem to have an obvious physical meaning.

3. LOCAL LINEARIZATION

It was shown by LIAPOUNOFF [8] that questions of stability of a steady state could be determined by considering only the linear equations describing small departures from the steady state. This theorem has been applied to the stirred tank reactor [1, 2] and the argument presented here simply applies this to the more general system under discussion.

The equations (2.5) and (2.6) are of the form

$$\dot{\xi} = \overline{P}(\xi, \eta), \quad \dot{\eta} = \overline{Q}(\xi, \eta) \qquad (3.1)$$

and the steady state ξ_s, η_s is such that $\overline{P}(\xi_s, \eta_s) = \overline{Q}(\xi_s, \eta_s) = 0$. In the neighbourhood of this steady state one may write

$$\left.\begin{aligned} \frac{d}{dt}(\xi - \xi_s) &= \\ &(\overline{P}_\xi)_s(\xi - \xi_s) + (\overline{P}_\eta)_s(\eta - \eta_s) + O_2 \\ \frac{d}{dt}(\eta - \eta_s) &= \\ &(\overline{Q}_\xi)_s(\xi - \xi_s) + (_\eta)_s(\overline{Q}\eta - \eta_s) + O_2 \end{aligned}\right\} \qquad (3.2)$$

where $(\overline{P}_\xi)_s$ is $\frac{\partial \overline{P}}{\partial \xi}$ evaluated at ξ_s, η_s etc. and O_2 denotes terms of the order of squares and products of $(\xi - \xi_s)$ and $(\eta - \eta_s)$. The linear system of equations obtained by neglecting the O_2 terms is stable only if

$$-(\overline{P}_\xi)_s - (Q_\eta)_s > 0 \qquad (3.3)$$

$$(\overline{P}_\xi)_s(\overline{Q}_\eta)_s - (\overline{P}_\eta)_s(\overline{Q}_\xi)_s > 0 \qquad (3.4)$$

To apply these criteria, three dimensionless numbers which characterize the steady state are introduced. They are :

$$\alpha = (P_\xi)_s = \frac{V}{q}\frac{\partial R}{\partial x} = \frac{\text{increase in reaction rate with increasing } x}{\text{increase in flow rate of } x \text{ with increasing } x}$$

$$\beta = (U_\eta)_s = \frac{V}{qc\rho}\frac{\partial U^*}{\partial T} = \frac{\text{increase of heat rejection rate per unit temp. rise}}{\text{increase of heat content flow per unit temp. rise}}$$

$$\gamma = (-P_\eta)_s = \frac{-V(-\Delta H)}{qc\rho}\frac{\partial R}{\partial T} = \frac{\text{increase of heat envolved by reaction per unit temp. rise}}{\text{increase of heat content flow per unit temp. rise}}$$

Then applying the conditions (3.3) and (3.4) to equations (2.5) and (2.6) stability requires

$$1 + \alpha + 1 + \beta > \gamma \qquad (3.5)$$

$$(1 + \alpha)(1 + \beta) > \gamma \qquad (3.6)$$

These conditions may be given a geometrical representation if α, β, γ are thought of as co-ordinates of a point S in α, β, γ space. The surface E defined by

$$d_e \equiv 1 + \alpha + 1 + \beta - \gamma = 0 \qquad (3.7)$$

is a plane intersecting the co-ordinate planes $\alpha = 0$ and $\beta = 0$ in the straight lines $\gamma = 2 + \beta$, $\gamma = 2 + \alpha$ respectively. The surface F defined by

$$d_f \equiv (1 + \alpha)(1 + \beta) - \gamma = 0 \qquad (3.8)$$

is an hyperboloid intersecting planes of constant α or β in straight lines. The quantities d_e and d_f are the distances from the point S to the surfaces E and F respectively and the condition for stability is that these should both be positive. It will be convenient to divide the α, β, γ space up into one stable and three unstable regions as follows

Region	D_s	D_1	D_2	D_3
Sign of d_e	+	−	+	−
Sign of d_f	+	+	−	−

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More information about the behaviour in the neighbourhood of a steady state can be extracted from this local linearization. The solution of equations (3.2) is

$$\xi - \xi_s = C_1 \exp \omega_1 t + C_2 \exp \omega_2 t \qquad (3.9)$$
$$\eta - \eta_s = C_3 \exp \omega_1 t + C_4 \exp \omega_2 t$$

where ω_1 and ω_2 are roots of the quadratic

$$\omega^2 + d_e \omega + d_f = 0 \qquad (3.10)$$

and the constants C_3 and C_4 are not independent of C_1 and C_2. The stability condition $d_e > 0$, $d_f > 0$ simply ensures that the real parts of ω_1 and ω_2 shall be negative. If ω_1 and ω_2 are complex conjugates the right hand sides of equations (3.9) are damped oscillations and might be written in the form

$$\xi - \xi_s = A_1 \sin(\mu t + \phi_1) \exp(\lambda t)$$
$$\eta - \eta_s = A_2 \sin(\mu t + \phi_2) \exp(\lambda t)$$

When the approach to the steady state is of this oscillatory character the critical point ξ_s, η_s is called a focus (Fig. 2a); it is stable or unstable according as $\lambda < 0$ or $\lambda > 0$. The stable case corresponds exactly to the motion of a simple harmonic pendulum with less than critical damping; it performs an infinite number of oscillations but their amplitude decreases exponentially with time (Fig. 2b). If $\lambda = 0$ (i.e., $d_e = 0$) a small disturbance around the origin would persist as a simple harmonic oscillation, neither tending to grow nor decreasing in amplitude. The critical point is then called a vortex, and it stands at a transition from stability to instability. If both roots ω are real and of the same sign, the motion has no oscillatory character and corresponds to an overdamped pendulum. It is stable or unstable according as the roots are negative or positive. The critical point is known as a node in this case (Fig. 2c, d).

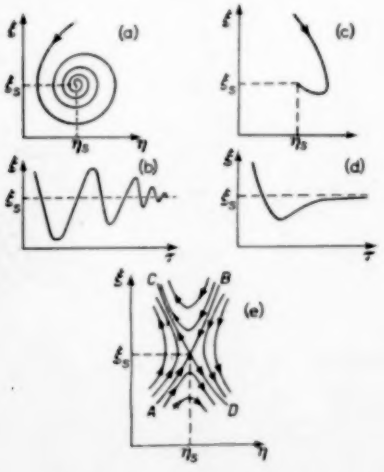

FIG. 2. Types of critical point.

If both roots are real but of opposite sign the critical point is called a saddle-point or col. Making use of the dependence of C_3 and C_4 on C_1 and C_2 alluded to above, the solution of the linearized equations may be written

$$\xi - \xi_s = C_1 \gamma \exp(-\omega_1 t) + C_2 \gamma \exp(+\omega_2 t)$$
$$\eta - \eta_s = C_1 (1 + \alpha - \omega_1) \exp(-\omega_1 t) + C_2 (1 + \alpha + \omega_2) \exp(+\omega_2 t)$$

where now ω_1 and ω_2 are both positive. Thus if originally $(\xi - \xi_s)/(\eta - \eta_s) = \gamma/(1 + \alpha - \omega_1)$ one may set $C_2 = 0$ and both ξ and η tend exponentially towards ξ_s and η_s and the ratio $(\xi - \xi_s)/(\eta - \eta_s)$ does not change (curves A and B of Fig. 2e). On the other hand if $(\xi - \xi_s)/(\eta - \eta_s) = \gamma/(1 + \alpha + \omega_2)$ originally ξ and η tend exponentially away from ξ_s, η_s (curves C and D of Fig. 2e). From any other original point C_2 cannot be zero so that though $\xi - \xi_s$ or $\eta - \eta_s$ may decrease at first the positive exponential ultimately dominates and the condition departs from the steady state. In the ξ, η plane the trajectories appear as in Fig. 2e and the curves AB and CD are known as the separatrices.

The condition that both the roots of equation (3.10) should be real is that $d_e^2 > 4 d_f$ i.e.

$$(\alpha - \beta)^2 - 2(\alpha + \beta)\gamma + \gamma^2 > 0 \qquad (3.11)$$
$$\alpha^2 + \beta^2 + \gamma^2 > 2(\alpha\beta + \beta\gamma + \gamma\alpha)$$

In the α, β, γ space this is the exterior of a parabolic surface touching the planes $\alpha = 0$ and $\gamma = 0$ along the lines $\gamma = \beta$ and $\gamma = \alpha$ and the surface F along its intersection with the plane E. A section of these surfaces by a plane of constant β is shown in Fig. 3.

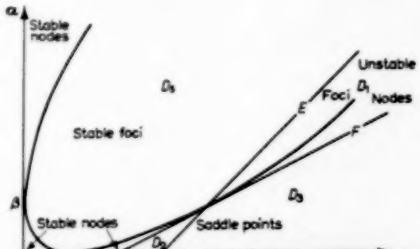

FIG. 3. Nature of the critical points as functions of the parameters α, β, γ.

4. MODES OF PERFECT CONTROL

The differential equations (2.5) and (2.6) contain two variables

ξ, the concentration
η, the temperature

and a number of parameters

ξ_{i0}, the inlet concentrations
η_0, the inlet temperature
η_c, the temperature of the coolant
q_c, the flow rate of the coolant,

the last two appearing in the function $U(\eta)$. At a given steady state all these quantities have fixed values and it is proposed to control this steady state by measuring the deviations of one of the variables and using this measurement to alter one of the parameters in such a way that the steady state values are restored. The flow rate of the coolant immediately suggests itself as the parameter to control but at this stage the question is left open whether the deviations of ξ or η should be used for this. There are three distinct types of perfect control to consider, in which the parameter deviation is made proportional to the value, the derivative or the integral of the variable deviation. Only perfect control, in which this is attained without time lags, will be considered in this paragraph, the consideration of imperfect control being the concern of par. 6. Moreover the possibility of control from the local linearization only will be studied, for if it is not possible to render a steady state stable locally it will certainly not be possible in the large.

Let ξ_s, η_s be the concentration at a steady state and the parameters α, β, γ be defined as before and define the parameter

$$\delta = \left(\frac{\partial U}{\partial q_c}\right)_s = \text{rate of change of heat rejection with respect to variation of coolant flow rate.}$$

Using an asterisk to denote the deviations of any quantity from its steady state value the local linearization of equations (2.5) and (2.6) is

$$\dot{\xi}^* = -(1+\alpha)\,\xi^* + \gamma\,\eta^* \tag{4.1}$$

$$\dot{\eta}^* = -\alpha\,\xi^* - (1+\beta-\gamma)\,\eta^* - \delta\,q_c^* \tag{4.2}$$

The method of control is to put q_c^* proportional to ξ^* or η^* or to one of their derivatives or integrals. The possibilities are as follows; in which for later simplicity the proportionality constant has been written K/δ.

Mode of control	*Proportional*	*Derivative*	*Integral*
q_c^*	$(K/\delta)\,\eta^*$ or ξ^*	$(K/\delta)\,\frac{d\eta^*}{dt}$	$(K/\delta)\int \eta^*\,dt$
$\bar{q}_c^*$	$(K/\delta)\,\bar{\eta}^*$ or $\bar{\xi}^*$	$(K/\delta)\,p\,\bar{\eta}^*$	$(K/\delta)\,\bar{\eta}^*/p$

In the second line of this table is given the relations between the Laplace transforms of the variables, which are denoted by a bar. The Laplace transform is defined by

$$\bar{\xi}^* = \int_0^\infty e^{-p\tau}\,\xi^*(\tau)\,d\tau \tag{4.3}$$

and applying the Laplace transformation to the equations (4.1) and (4.2) there results

$$(p+1+\alpha)\,\bar{\xi}^* - \gamma\,\bar{\eta}^* = (\xi^*)^\circ \tag{4.4}$$

$$\alpha\bar{\xi}^* + (p+1+\beta-\gamma)\,\bar{\eta}^* = (\eta^*)^\circ - \delta\,\bar{q}_c^* \tag{4.5}$$

where $(\xi^*)^\circ$ and $(\eta^*)^\circ$ are the initial perturbations. If q_c is uncontrolled, i.e. $\bar{q}_c^* = 0$ the solution is

$$\Delta(p)\,\bar{\xi}^* = (p+1+\beta-\gamma)\,(\xi^*)^\circ + \gamma\,(\eta^*)^\circ \tag{4.6}$$

$$\Delta(p)\,\bar{\eta}^* = (p+1+\alpha)\,(\eta^*)^\circ - \alpha\,(\xi^*)^\circ$$

where

$$\Delta(p) = p^2 + d_e\,p + d_j \tag{4.7}$$

the determinant of the left hand side is a quadratic identical with (3.10). The inversion of these relations gives the solution (3.9) and the condition for stability is again that the roots of (4.7) should have negative real parts. When q_c is controlled, one of the relations from the above table is inserted into (4.5) and the polynomial $\Delta(p)$ is correspondingly modified. This will be done for the various modes of control mentioned above.

(i) *Proportional control on* ξ^*. Here $\bar{q}_c^* = (K/\delta)\,\bar{\xi}^*$ and the determinant Δ becomes

$$\Delta(p) \equiv \begin{vmatrix} p+1+\alpha & -\gamma \\ K+\alpha & p+1+\beta-\gamma \end{vmatrix} = p^2 + d_e p + d_j + \gamma K$$

The condition for stable control is $d_e > 0$, $d_j + \gamma K > 0$, so that if $d_e < 0$ (i.e. the operating point S is in D_1 and D_3) control can never be achieved. If $d_e > 0$ however, it is only necessary

to make K positive and $K > -d_f/\gamma$ for the controlled point to be stable.

(ii) *Proportional control on* η^*. Here $\bar{q}_c^* = (K/\delta)\,\bar{\eta}^*$ and

$$\Delta \equiv p^2 + (d_e + K)\,p + (d_f + K\,(1 + \alpha)).$$

Thus by making $K > \max\{-d_e, -d_f/(1+\alpha)\}$ both coefficients can be made positive and stability is assured.

A similar analysis of derivative and integral modes shows that the following situation obtains with regard to local accessibility to control. A denotes that if the operating point $S\,(\alpha, \beta, \gamma)$ is in the region, control can be attained, N that it cannot.

Mode	*Proportional*			*Derivative*			*Integral*		
Region	D_1	D_2	D_3	D_1	D_2	D_3	D_1	D_2	D_3
Control on ξ^*	N	A	N	A	N	N	N	N	N
Control on η^*	A	A	A	A	A	A	N	N	N

It is clear from this table that it is preferable to control on measurements of temperature deviation and that integral control is invariably too sluggish to succeed.

Before passing on to imperfect control it is interesting to consider whether if all three modes are present the first two can be made to overcome the slowness of the third. For this, put $\bar{q}_c^* = (K_1 + K_2\,p + K_3/p)\,(\eta^*/\delta)$ and obtain the cubic,

$$\Delta \equiv (1 + K_2)\,p^3 + \{d_e + K_1 + K_2\,(1+\alpha)\}\,p_2 + \{d_f + K_3 + K_1\,(1+\alpha)\}\,p + K_3\,(1+\alpha).$$

This has stable roots if $K_3 > 0$, $(1 + K_2) > 0$, $d_e + K_1 + K_2\,(1+\alpha) > 0$ and $\{d_e + K_1 + K_2\,(1+\alpha)\}\{d_f + K_3 + K_1\,(1+\alpha)\} > K_3\,(1+K_2)\,(1+\alpha)$. This can be achieved by making K_1 and K_2 sufficiently large. On the other hand, if K_1 and K_2 are fixed the first and last conditions put a bound on K_3, the amount of integral control that can be tolerated.

5. Imperfect Control

A servo-mechanism so perfect that signals of temperature deviation produce proportional changes in the flow rate of the coolant without either delay or error does not exist. In practice a thermocouple reading will actuate a motor which will turn a valve and at all stages there will be errors and delays. Following the accepted practice of servo-mechanism theory, all these factors may be lumped into one transfer function, writing

$$\delta\,\bar{q}_c^* = K\,G\,(p)\,\bar{\eta}^*. \tag{5.1}$$

The way in which this transfer function is constructed is described in the texts (see, for example, Chestnut and Mayer [4]) and it is not our concern to discuss this here. It is important, though, to find out whether the time lag of an imperfect system which is ultimately a proportional controller can destroy the possibility of control. It is shown in Chestnut and Mayer that a transfer function ultimately giving proportional response can be of the form

$$G\,(p) = M\,(p)/N\,(p) \tag{5.2}$$

where

$$M\,(p) \equiv p^m + m_1 p^{m-1} + \ldots + m_m = (p + \mu_1)\,(p + \mu_2)\ldots(p + \mu_m)$$

and (5.3)

$$N\,(p) \equiv p^n + n_1 p^{n-1} + \ldots + n_n = (p + \nu_1)\,(p + \nu_2)\ldots(p + \nu_n)$$

The μ_1 and ν_1 are reciprocals of certain time constants of the mechanism and are necessarily positive or the servo-mechanism itself would be unstable. Thus the coefficients m_i and n_i satisfy the Routh–Hurwitz conditions

$$m_1 > 0, \begin{vmatrix} m_1 & 1 \\ m_3 & m_2 \end{vmatrix} > 0, \begin{vmatrix} m_1 & 1 & 0 \\ m_3 & m_2 & m_1 \\ m_5 & m_4 & m_3 \end{vmatrix} > 0, \text{ etc.} \tag{5.4}$$

Such a servo-mechanism inserted in our system would give stable control if the numerator $\Delta\,(p)$ of the rational function

$$(p + 1 + \alpha)\{p + 1 + \beta - \gamma + K\,G\,(p)\} + \alpha\,\gamma$$

has all its roots with negative real part. Now

$$\begin{aligned}\Delta(p) &= (p^2 + d_e p + d_f)\, N(p) \\ &\quad + K\,(p + 1 + \alpha)\, M(p) \\ &= p^{n+2} + (d_e + n_1)\, p^{n+1} \\ &\quad + (n_2 + d_e n_1 + d_f)\, p^n + \ldots + d_f n_n \\ &\quad + K\{p^{m+1} + [m_1 + 1 + \alpha]\, p^m \\ &\quad + [m_2 + (1 + \alpha)\, m_1]\, p^{m-1} \\ &\quad + \ldots (1 + \alpha)\ m_m\} \\ &= p^l + l_1 p^{l-1} + \ldots + l_l\end{aligned}$$

where $l = \max\ (m + 1,\ n + 2)$. If $m \geqslant n + 1$ all the coefficients will be of the form $l_i = N_i + KM_i$ where $M_i = m_i + m_{i-1}\,(1 + \alpha)$. From the Routh–Hurwitz determinant of order q a term $K^q \times$ (the R.H. determinant of the $\mathbf{M}_i$) may be taken out and all other terms will be of order K^{q-1} or less. For example, if $m = n + l$, $q = 2$,

$$\begin{vmatrix} N_1 + KM_1 & 1 + K \\ N_3 + KM_3 & N_2 + KM_2 \end{vmatrix} = K^2 \begin{vmatrix} M_1 & 1 \\ M_3 & M_2 \end{vmatrix}$$

$$+ K \left\{ \begin{vmatrix} M_1 & 1 \\ M_3 & N_2 \end{vmatrix} + \begin{vmatrix} N_1 & 1 \\ N_1 & M_2 \end{vmatrix} \right\} + \begin{vmatrix} N_1 & 1 \\ N_3 & N_2 \end{vmatrix}$$

But the determinant of the M_i is the R.H. determinant of the polynomial $(p + 1 + \alpha)\, M(p)$ and so is positive. Hence by choosing a sufficiently large K, the R.H. determinants of the l_i can be made positive and stability assured.

If $m = n$,

$$l_1 = d_e + n_1 + K,\ l_2 = n_2 + n_1 d_e + d_f + K\,(m_1 + 1 + \alpha),$$

$$l_{r+2} = n_{r+2} + d_e n_{r+1} + d_f + K\,[m_{r+1} + (1 + \alpha)\, m_r].$$

The factor of K^{q+1} in the $(q + 1)^{\text{th}}$ order R.H. determinant is

$$\begin{vmatrix} 1 & 0 & 0 & . & . \\ m_2 + (1+\alpha)m_1 & m_1 + (1+\alpha)m_0 & 1 & . & . \\ m_4 + (1+\alpha)m_3 & m_3 + (1+\alpha)m_2 & m_2 + (1\alpha)m_1 & . & . \\ . & . & . & . & . \end{vmatrix}$$

which, since the first line is zero except for its first term, is simply the qth order R.H. determinant of $(p + 1 + \alpha)\, M(p)$ and so is positive. Again, a sufficiently large value of K will succeed in control.

The conditions, $m = n + 1$ and $m = n$, may be interpreted to mean that the ultimately proportional control is initially derivative or proportional. It is, however, more likely that the response would initially be more sluggish, for example, corresponding to integral control, i.e., $m = n - 1$. In this case there will be limitations on the coefficients n_i which involves the reciprocals of the time lags of the system. Since the first term in which K can appear to be of service in forcing it to be positive is the second, there is a first condition, $d_e + n_1 > 0$, which must be satisfied by making the time lags ν_i^{-1} so small that the sum of their reciprocals n_1 is greater than $-\,d_e$. The second condition is

$$K\,(n_1 + d_e - 1 - \alpha - m_1) + (n_1 n_2 - n_3) + d_e n_1\,(n_1 + d_e) + d_e d_f > 0 \qquad (5.6)$$

which since $K > 0$ imposes a yet stronger condition on the ν_i^{-1}. However this condition can always be satisfied by making the ν_i^{-1} sufficiently small, for the term $(n_1 n_2 - n_3)$ is of order -3 in them and being a R.H. determinant is positive and can be made to dominate the expression. It is clear that K and the n_i are related in a much more complex fashion and control cannot be attained simply by increasing the gain K. It is first necessary to insure that the time lags make the coefficient of K positive, e.g. in (5.6), $n_1 > 1 + \alpha + m_1 - d_e$ if increasing K is to be of any service.

In the case $m = n - 2$ a much more serious restriction appears for while again the first condition is $d_e + n_1 > 0$, the second is

$$K < (n_1 n_2 - n_3) + d_e n_1\,(n_1 + d_e) + d_e d_f$$

which is actually a bound on the possible gain K. Thus for $m \leqslant n - 2$ stability can only be assured by making the time lags of the system sufficiently small and an increase in the gain K will actually induce instability. Two examples may be used to illustrate this.

Let

$$G(p) = \frac{(p + \mu_1)\,(p + \mu_2)}{(p + \nu_1)\,(p + \nu_2)} \qquad (5.7)$$

be the transfer function of a servo-mechanism both initially and ultimately proportional. The characteristic polynomial

$$\Delta(p) \equiv p^4 + p^3(\nu_1 + \nu_2 + d_e + K) + p^2\{\nu_1\nu_2 + (\nu_1 + \nu_2)d_e + d_f + K(\mu_1 + \mu_2 + 1 + \alpha)\} + p[\nu_1\nu_2 d_e + (\nu_1 + \nu_2)d_f + K\{\mu_1\mu_2 + (1 + \alpha)(\mu_1 + \mu_2)\}] + \{\nu_1\nu_2 d_f + K(1 + \alpha)\mu_1\mu_2\}$$

The first and fourth R.H. determinants give

$$\nu_1 + \nu_2 + d_e + K > 0 \text{ and}$$
$$\nu_1\nu_2 d_f + K(1 + \alpha)\mu_1\mu_2 > 0$$

which can be satisfied for sufficiently large K. The leading terms in the second and third conditions are

$$K^2(\mu_1 + \mu_2 + 1 + \alpha) \text{ and}$$
$$K^3(\mu_1 + \mu_2 + 1 + \alpha)\{\mu_1\mu_2 + (1 + \alpha)(\mu_1 + \mu_2)\}$$

so that by making K sufficiently large these conditions too can be fulfilled, however large the time lags may be (i.e., however small the ν_i and μ_i). It is to be noticed, however, that the coefficients of K contain the sum and product of μ_1 and μ_2. Thus it will be much easier to attain control if the μ_1 are large, i.e., the corresponding time lags small.

In the case of an initially integral controller

$$G(p) = \frac{p + \mu}{(p + \nu_1)(p + \nu_2)} \tag{5.8}$$

$$\left.\begin{aligned} &\Delta(p) = p^4 + l_1p^3 + l_2p^2 + l_3p + l_4 \\ &\text{where } l_1 = \nu_1 + \nu_2 + d_e \\ &l_2 = \nu_1\nu_2 + (\nu_1 + \nu_2)d_e + d_f + K \\ &l_3 = \nu_1\nu_2 d_e + (\nu_1 + \nu_2)d_f K(1 + \alpha + \mu) \\ &l_4 = \nu_1\nu_2 d_f + K\mu(1 + \alpha) \end{aligned}\right\} \tag{5.9}$$

and the Routh–Hurwitz conditions are

$$l_1 = \nu_1 + \nu_2 + d_e > 0 \tag{5.10}$$

$$\begin{vmatrix} l_1 & 1 \\ l_3 & l_2 \end{vmatrix} > 0 \tag{5.11}$$

$$\begin{vmatrix} l_1 & 1 & 0 \\ l_3 & l_2 & l_1 \\ 0 & l_4 & l_3 \end{vmatrix} > 0 \tag{5.12}$$

$$l_4 = \nu_1\nu_2 d_f + K\mu(1 + \alpha) > 0 \tag{5.13}$$

For any given set of values K, μ, α, β, γ these inequalities define a region of the ν_1, ν_2 plane within which the point $N(\nu_1, \nu_2)$ characterizing the time lags of the system must lie. Fig. 4 shows this: (5.10) is a straight line bounding N away from the origin, (5.13) is a rectangular hyperbola and (5.11) and (5.12) give curves of similar shape to the hyperbola of which only one is shown. The region is symmetrical about the line $\nu_1 = \nu_2$ and it must include at least the region defined by

$$\nu_1 + \nu_2 > -d_e + 1 + \alpha + \mu,$$
$$\nu_1\nu_2 > K\mu(1 + \alpha)/(-d_f) \tag{5.14}$$

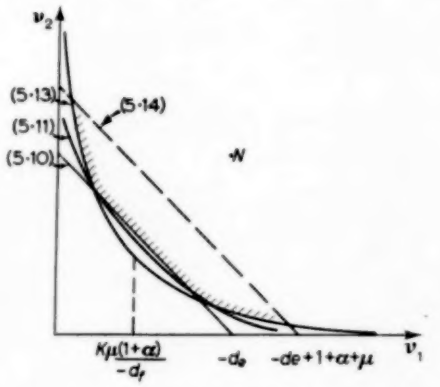

FIG. 4. Restrictions on the time lags of an imperfect proportional controller.

6. A MEASURE OF LOCAL CONTROL

It is convenient to introduce a numerical measure for the degree of stability of a steady state and hence of the effectiveness of control. Suppose that $W(t)$ is the response of one of the system variables to a unit disturbance in one of the others, then

$$I = \int_0^\infty |W(t)|^2\, dt \tag{6.1}$$

is a measure of the total disturbance caused by this impulse. For example if in the uncontrolled equation one puts $(\eta^*)_0 = 1$ the responses $W_{\xi\eta}$ and $W_{\eta\eta}$ of the variables ξ and η are

$$W_{\xi\eta}(t) = \left(\frac{\gamma}{\omega_1 - \omega_2}\right)(e^{\omega_1\tau} - e^{\omega_2\tau})$$

$$W_{\eta\eta}(t) = \left(\frac{\gamma}{\omega_1 - \omega_2}\right)\{(\omega_1 + 1 + \alpha)e^{\omega_1\tau} - (\omega_2 + 1 + \alpha)e^{\omega_2\tau}\}$$

If and only if ω_1 and ω_2 have negative real part the integrals I will converge and

$$I_{\xi\eta} = \gamma^2/2\, d_e\, d_f$$

$$I_{\eta\eta} = \{d_f + (1+\alpha)^2\}/2\, d_e\, d_f$$

The stability of the steady state is thus greater or less according as the product $d_e\, d_f$ is large or small and this product gives a useful measure. Further, the attainment of control Γ may be defined by

$$\Gamma = 1 - \frac{(d_e\, d_f)\text{ uncontrolled}}{(d_e\, d_f)\text{ controlled}} \qquad (6.2)$$

a quantity which is zero for no control and unity for perfect control. For example, for the control of q_c^* on η^*

$$\Gamma = 1 - \left(1 + \frac{K}{d_e}\right)^{-1} \left(1 + \frac{K(1+\alpha)}{d_f}\right)^{-1}$$

$$\doteq 1 - \frac{d_e\, d_f}{K^2(1+\alpha)}$$

Γ has the physical meaning that it is the difference between the total disturbance for controlled and uncontrolled states as a fraction of the uncontrolled disturbance. For an originally unstable state this meaning is lost since the total disturbance is then infinite but the measure defined above in (6.2) retains a meaning for sufficiently good control approaching unity as the control is increased. A measure of control on similar lines to this has been introduced by BILOUS, BLOCK and PIRET [3] in their treatment of the locally linearized case.

CONCLUSIONS

In this paper the application of the method of local linearization to the analysis of chemical reactor control has been discussed. It may be used to determine the stability of the immediate neighbourhood of a steady state, and hence the possibility of control by various means. For clearly, if stability is not attained in such a neighbourhood, there is no hope of control in any larger sense. It is found preferable to measure the deviation of the reactor temperature from that of the steady state and use this signal to control the rate of cooling. If the response of a perfect controller is proportional to this deviation or to its derivative, control may always be attained by sufficient amplification of the signal. A response proportional to the integral of the deviation, however, is too sluggish to be effective. With imperfect control, when there are certain time lags in the system, it has been shown that, even when the response is ultimately proportional to the deviation, these time lags must be kept below certain bounds.

LIST OF SYMBOLS

A_j = Stoicheiometric coefficients (2)

D_s, D_1, D_2, D_3 = Regions of α, β, γ space (3)

$G(p)$ = Transfer function (5)

ΔH = Heat of reaction (2)

$$I = \int_0^\infty |W(t)|^2\, dt \quad (7)$$

K, K_1, K_2, K_3 = Proportionality constants (4)

$M(p)$ = Numerator of $G(p)$ (5)

$N(p)$ = Denominator of $G(p)$ (5)

$\overline{P}$, $\overline{Q}$ = Abbreviation for r.h.s. of equations (3)

R = Reaction rate (2)

T = Temperature

U^* = Heat transfer function (2)

$U = VU^*/qx_0(-\Delta H)$ reduced h.t.f. (2)

V = Volume of reactor (2)

$W(t)$ = Response to unit disturbance (6)

X, X_j = Chemical species (2 and 14)

c = Specific heat (2)

$d_e = 1 + \alpha + 1 + \beta - \gamma$ (3)

$d_f = (1+\alpha)(1+\beta) - \gamma$ (3)

m_r = Coefficients in $M(p)$ (5)

n_r = Coefficients in $N(p)$ (5)

p = Transform variable

q = Flow rate of reactants (2)

q_c = Flow rate of coolant (2)

t = Time (2)

x = Concentration of X (2 and 14)

Γ = Measure of control (6)

P = Reduced reaction rate (2)

α, β, γ = Stability parameters (3)

$\delta = (\partial U/\partial q_c)_s$ (4)

$\eta = c\rho T/x_0(-\Delta H)$, reduced temperature (2)

$\xi = x/x_0$, reduced concentration (2)

μ_i = Roots of $M(p)$

ν_i = Roots of $N(p)$

ρ = Density (2)

$\tau = qt/V$, reduced time (2)

ω = Roots of characteristic equation (3 and 6)

Suffixes and affixes

c = Coolant

j = No. of species ($j = 1, \ldots n$)

$^\circ$ = Initial value

$_s$ = Steady state value

* = Deviation from steady state (4)

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An analysis of chemical reactor stability and control—II*

The evolution of proportional control

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Abstract—In this part it is assumed that the control system receives signals of the deviation of reactor temperature and uses them to give a perfect proportional control of the rate of cooling. It has already been shown that control cannot be attained until the proportionality constant is great enough but it appears here that even when this minimum value has been exceeded, the control may only extend to comparatively small disturbances. To see how this comes about, it is necessary to follow the behaviour of the reactor through the variation of the control parameter, and it is shown that the methods of non-linear mechanics make this possible without excessive labour. There comes a point, however, when some computation is necessary and this is exemplified in a complete description of a simple system.

Résumé—Dans cet article les auteurs supposent que l'appareil de contrôle reçoit les signaux des variations de t° du réacteur et les utilise pour donner un contrôle proportionnel, parfait de la vitesse de refroidissement. On a déjà montré que le contrôle ne peut être obtenu tant que la constante de proportionnalité n'est pas suffisamment élevée. Mais il semble ici que même lorsque la valeur critique n'a pas été dépassée, le contrôle ne peut s'étendre qu'à des perturbations relativement faibles. Pour vérifier ce comportement, il est nécessaire de suivre la marche du réacteur pendant la variation du paramètre de contrôle ; les auteurs ont montré que les méthodes à mécanisme non linéaire, rendent ceci possible sans trop de travail. Mais il peut arriver que certains calculs soient nécessaires, et ceci est illustré dans une description complète du système simple.

Zusammenfassung—In dieser Arbeit ist angenommen, dass das Regelsystem Signale über die Abweichung der Reaktortemperatur empfängt und hiernach eine vollständige Proportionalregelung der Kühlgeschwindigkeit durchführt. Es ist schon gezeigt worden, dass eine Regelung nicht erzielt werden kann, ohne dass die Proportionalitätskonstante gross genug ist ; hier scheint sogar nach Überschreiten dieses Minimalwertes eine Regelung nur bis zu vergleichsweise kleinen Störungen ausführbar zu sein. Um zu sehen, wie es dazu kommt, muss man das Verhalten des Reaktors bei Variation des Regelungsparameters verfolgen und es zeigt sich, dass die Methoden der nichtlinearen Mechanik dieses ohne allzu grossen Rechenaufwand gestatten. Indessen geht es nicht ohne Rechnung ab und diese wird an der vollständigen Beschreibung eines einfachen Systems gezeigt.

7. THE HEAT TRANSFER FUNCTION

THE discussion so far has concerned itself wholly with the local properties of the functions involved and before going on to more general considerations in the large, the heat transfer function demands a little consideration. In fact, all that is required is a function expressing the rate of heat rejection in terms of η the temperature inside the reactor and η_c and q_c, the inlet temperature and flow rate of the coolant, and this might well be an empirically determined one. Without implying any restriction on the method here presented it will be convenient to derive a fairly simple approximate expression for U. In the first place, it will be supposed that it is proportional to the difference between the reactor temperature and

*For ease of reference, the numbering of the sections and figures is continuous with Part I.
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and the mean coolant temperature, $\bar{\eta}_c$, and, secondly, following respected correlations, to the four-fifth power of the flow rate. Thus

$$U(\eta) = A\left(\frac{q_c}{q}\right)^{4/5}(\eta - \bar{\eta}_c) \tag{7.1}$$

Again, the total rise in temperature, is $2(\bar{\eta}_c - \eta_c)$, so that since the heat rejected goes to warm up the coolant

$$U(\eta) = 2B\left(\frac{q_c}{q}\right)(\bar{\eta}_c - \eta_c) \tag{7.2}$$

Eliminating $\bar{\eta}_c$ from these two equations

$$U(\eta;\, \eta_c,\, q_c) = AB\left(\frac{q_c}{q}\right)(\eta - \eta_c)\Big/\left\{A + B\left(\frac{q_c}{q}\right)^{1/5}\right\} \tag{7.3}$$

A is a constant involving the cooling area and materials of the heat exchanger, B involves the heat capacity of the coolant.

For the perfect proportional control assumed here, the deviation of q_c from its steady state value q_{cs} is to be made proportional to the deviation of temperature η from the desired steady state value η_s. Naturally this must be within the range of movement of a control valve and it is assumed for simplicity that in the steady state the flow rate is half its maximum. Thus

$$\frac{q_c}{q} = \frac{q_{cs}}{q} + K(\eta - \eta_s) \text{ for } |\eta - \eta_s| \leqslant \eta_r \tag{7.4}$$

where $\eta_r = \dfrac{1}{K}\left(\dfrac{q_{cs}}{q}\right)$ is the half range of temperature which causes the valve to move. For

$$\eta \leqslant \eta_s - \eta_r,\ \frac{q_c}{q} = 0, \tag{7.5}$$

while for

$$\eta \geqslant \eta_s + \eta_r,\ \frac{q_c}{q} = 2\frac{q_{cs}}{q} \tag{7.6}$$

Introducing (7.4) into the expression (7.3) for U and expanding in a Taylor series

$$U(\eta) = \left[\frac{AB\,q_{cs}/q}{A + B(q_{cs}/q)^{0.2}}\right](\eta - \eta_c) + KAB\left[\frac{A + \frac{1}{5}B(q_{cs}/q)^{0.2}}{\left[A + \frac{1}{5}B(q_{cs}/q)^{0.2}\right]^2}\right](\eta - \eta_c)(\eta - \eta_s) + \ldots \tag{7.7}$$

when $|\eta_s - \eta| \leqslant \eta_r$. This expression, which can now be written with convenient simplicity, will be of good accuracy since the $(q_c/q)^{0.2}$ in the denominator is of comparatively little effect. Therefore

$$U(\eta) = \begin{cases} U_m(\eta - \eta_c), \\ U_s(\eta - \eta_c) + k(\eta - \eta_c)(\eta - \eta_s), \\ 0, \end{cases} \quad \text{when} \quad \begin{cases} \eta \geqslant \eta_s + \eta_r \\ |\eta - \eta_s| \leqslant \eta_r \\ \eta \leqslant \eta_s - \eta_r \end{cases} \tag{7.8}$$

Since $U_m - U_s = k\,\eta_r$, the function U depends on the proportionality constant k in a peculiar way, which is perhaps best illustrated by Fig. 5. For very high gains, k, this reduces to off–on control in which the slightest drop in temperature shuts off the coolant and a slight rise opens the valve fully. This represents the limit of this form of control and will be considered in par. 13. In the calculations which follow it will be assumed that the range of the valve is such as to make the quadratic expression (7.8) valid.

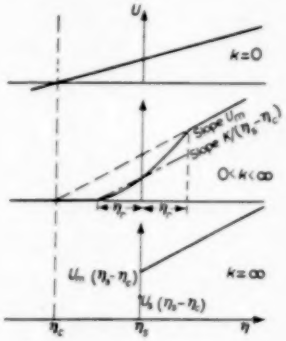

Fig. 5. The heat transfer function.

8. The Phase Plane

The notion of the phase plane has long been in use in non-linear mechanics for equations of the type (3.1). It allows one to get a picture of the behaviour of the system in the large, in contrast to the local linearization which gives information only in the neighbourhood of the critical point. Since time does not occur explicitly in equations (3.1), η may be taken as the independent variable so that

$$\frac{d\xi}{d\eta} = \frac{\dot{\xi}}{\dot{\eta}} = \frac{\overline{P}(\xi, \eta)}{\overline{Q}(\xi, \eta)} \tag{8.1}$$

which is a single non-linear equation for ξ as a function of η. The value of $d\xi/d\eta$ is unique at every point where $\overline{P}$ and $\overline{Q}$ do not simultaneously vanish; such points are called ordinary points. The values of ξ, η where $\overline{P} = \overline{Q} = 0$ are, of course the steady states already discussed and these are known as critical points of the phase plane. Starting from an ordinary point the equation (8.1) can be integrated and gives a curve in the phase plane, a trajectory, which represents the life history of the system. Integrating the pair of equations (3.1) and plotting ξ versus η would give the same curve but now a time scale could be marked on the trajectory. This may be illustrated from the series of figures derived for the special case discussed later. For example, consider the trajectory DA in Fig. 11 starting from the point $\xi = 0$, $\eta = 1{\cdot}75$. This represents the history of a reactor when initially the temperature is 1·75 and concentration of X zero and it is seen that the temperature rises only slightly while the concentration of X goes up to some 96 per cent of its inlet value and at this critical point the steady state is reached. To see how quickly this comes about one can compare the curves marked A in Fig. 10 (a) and (b) where the concentration and temperature are separately plotted against time. It is seen that the approach is quite rapid and smooth as is characteristic of a nodal critical point.

The phase plane representation enables one to make considerable qualitative predictions about the behaviour of the system without integrating the equations in detail. Much use of these so-called topological method will be made in par. 9 but it will be useful here to elucidate certain general points. It is first noticed that a trajectory must always remain within a finite part of the phase plane. For low temperatures $P \to 0$ and $U < 0$ so that by (2.6) $\dot{\eta} > 0$ while for high temperatures P and U are large and $\dot{\eta} < 0$. Thus at low temperatures the temperature always tends to increase and at high temperatures to decrease. Moreover when $\xi = 1$, $\dot{\xi} < 0$ and when $\xi = 0$, $P = 0$, and $\dot{\xi} = 1 > 0$ so that from the upper and lower ξ boundaries a trajectory always tends to move inwards. By the second theorem of Bendixson (see MINORSKY [10]* p. 78) it can be stated that any trajectory

either (i) approaches a critical point
or (ii) approaches a closed curve
or (iii) is itself a closed curve.

An example of (i) occurs in Fig. 11; Fig. 17, corresponding to a different value of the control parameter, illustrates (ii) and (iii). Here the trajectories starting from the points A and C wind around and gradually approach the closed curve DEF (shown as a broken line) the one from inside and the other from the outside. The closed curve DEF is itself a trajectory and is called a limit cycle. It represents a sustained oscillation of the temperature and composition and under the conditions represented by this figure the system will always tend to get into this state.

In a previous paragraph it was seen that through a saddle point there are four trajectories, two which approach it and two which diverge from it. The two which approach it must come from somewhere, either from an unstable critical point or limit cycle or from the boundary. For example, in Fig. 11, it is found by integrating backwards that these trajectories come from points F and G on the lower and upper boundaries. On the other hand the trajectories going outwards must take one of the three alternatives given above and in Fig. 11 one goes to the node at A and the other to the focus at C. As was pointed out previously [2], the separatrix FBG is of great importance for starting up the system. It divides the phase plane into two parts such that from any initial conditions represented by a point in the left half the low temperature steady state is approached, while from any conditions in the right half the high temperature steady state is attained.

9. THE PHASE PLANE WITH CONTROL

It is interesting to see what can be said about control without doing any detailed calculations.

*All references are listed at the end of Part I of this paper (p. 131).

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It will be seen that a very good general picture can be built up from quite general arguments about the disposition of the critical points in the phase plane. Such arguments are well known in non-linear mechanics under the name of topological arguments. This study, which is further augmented by some simple calculations in the next paragraph, is both valuable in itself and a necessary preliminary to the more detailed calculations described later.

If the expression for U derived in the previous paragraph is inserted into equation (2.6), the pair of equations for ξ and η are

$$\dot{\xi} = 1 - \xi - P(\xi, \eta) \tag{9.1}$$

$$\dot{\eta} = (1 + U_s)(\eta - \bar{\eta}) - k(\eta - \eta_c)(\eta - \eta_s) - P(\xi, \eta) \tag{9.2}$$

where $\bar{\eta} = (\eta_0 + U_s \eta_c)/(1 + U_s)$. Following the previous procedure ξ may be eliminated between the two equations giving

$$(1 + U_s)(\eta - \bar{\eta}) + k(\eta - \eta_c)(\eta - \eta_s) = P(\xi_s(\eta), \eta) \tag{9.3}$$

where the right hand side is again the curve R in Fig. 1. With $k = 0$ i.e. in the absence of control, the left hand side is the straight line L but with any $k > 0$ it is a quadratic curve intersecting L at $\eta = \eta_c$ and $\eta = \eta_s$, and increasing in curvature with increasing k. It is the intersection of these new curves, e.g. Q and Q', with R which determines the new steady states for the various k.

In the first place it is clear that unless η_s is a steady state temperature for the uncontrolled system it will not be the temperature at which the reactor will be controlled for all values of k, for the increasing curvature of Q will cause it to intersect R at a varying point always different from η_s unless L and R intersect there. If, however, η_s is the temperature of a steady state B of the uncontrolled system it will always be one for all k. The other critical points will move as for example when Q' cuts R at A' and C' but ultimately a sufficiently large k may give a single intersection such as is shown by the curve Q. Then there is some hope of having attained control in the large sense as well as locally.

To discover the position and nature of the critical points for all k it is convenient to reverse the procedure and determine the value of k which gives a critical point at a chosen temperature. From $\dot{\xi} = 0$, the relation $\xi = \xi_s(\eta)$, which must be satisfied for a critical point, may be obtained, and hence from (9.3) the value of k for which a critical point is at $\xi_s(\eta)$, η, namely

$$k = \frac{-P(\xi, \eta) + (1 + U_s)(\eta - \bar{\eta})}{(\eta - \eta_c)(\eta - \eta_s)} \tag{9.4}$$

Even if the more accurate expression (7.3) were used for U it would still be possible to solve for k without much trouble. Now that ξ and η are known so are the parameters α, β, γ and d_e, d_f associated with the critical point and so its nature and stability are determined.

To illustrate the procedure a simple example is introduced, which despite its apparent simplicity shows the quite intricate evolution of reactor control. Although the simple character of the example allows performance of some of the steps more easily, the method outlined here is not in any way restricted by the complexity of the rate equation, $P(\xi, \eta)$, and its adaptation will be immediately obvious to the reader. The example concerns a first order irreversible exothermic reaction, ξ being the concentration of the reactant X being destroyed. Since $(-\Delta H)$ was defined as the heat of reaction for the formation of X it must be taken as negative in the second equation thus changing the sign of the reaction term. Thus

$$P(\xi, \eta) = \xi \left[\exp\left\{50\left(\frac{1}{2} - \frac{1}{\eta}\right)\right\}\right] = \xi Y \tag{9.5}$$

and the equations are

$$\dot{\xi} = 1 - \xi - \xi Y \equiv \bar{P}(\xi, \eta) \tag{9.6}$$

$$\dot{\eta} = -2(\eta - \bar{\eta}) - k(\eta - \eta_s)(\eta - \eta_c) + \xi Y \equiv \bar{Q}(\xi, \eta) \tag{9.7}$$

If $\eta_c = \eta_0 = \bar{\eta} = 1{\cdot}75$ and $\eta_s = 2$ these equations have a critical point at $\xi = \frac{1}{2}$, $\eta = 2$. To fix ideas still further this may be regarded as a reaction taking place in a vessel of 50 l. capacity. If the flow rate q is 50 l/min the hold-up time or unit of τ time is 1 min. If the activation energy of the reaction is 20,000 cal/mole,

the unit of η corresponds to 200°K. The critical point of interest is thus at a temperature of 400°K or 127°C and with the reactant concentration in the tank at 50 per cent of its inlet value. Most of the concern is with the temperature range $\eta = 1{\cdot}75$–$2{\cdot}25$, i.e., from 27 to 227°C.

The parameters of the steady states are

$$\alpha = Y\,;\ \beta = 1 + k(2\eta - \eta_c - \eta_s)\,;$$
$$\gamma = 50\,\xi\,Y/\eta^2 \qquad (9.8)$$

At the point $\eta = 2$, where an attempt is being made to get control of the originally unstable steady state, $\alpha = 1$, $\beta = 1 + k/4$, $\gamma = 6{\cdot}25$ and

$$d_e = (k-9)/4 \qquad d_f = (2k-9)/4 \qquad (9.9)$$

Hence there is no hope of control until $k > 9$ when both d_e and d_f become positive and the point stable. Solving the quadratic, $\omega^2 + d_e\,\omega + d_f = 0$, at this point there are two roots

$$\omega_{1,2} = -\tfrac{1}{8}(k-9) \pm \tfrac{1}{8}\sqrt{(k-5)(k-45)} \qquad (9.10)$$

Thus the character of the controlled point is as given in the following table.

Range of k	*Nature*	*Stability*
0–4·5	Saddle-point	Unstable
4·5–5	Node	Unstable
5–9	Focus	Unstable
9–45	Focus	Stable
45–	Node	Stable

The technique just outlined for determining the moving critical points may be applied for by (9·6–9·8)

$$\xi_s(\eta) = 1/(1 + Y) \qquad (9.11)$$

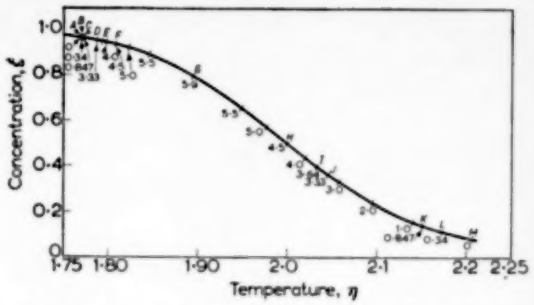

FIG. 6. Position of critical points for varying k.

$$k = \left\{\frac{Y}{1+Y} - 2(\eta - 1{\cdot}75)\right\}/(\eta - 1{\cdot}75)(\eta - 2) \qquad (9.12)$$

$$\left.\begin{aligned} \alpha &= Y \\ \beta &= 1 + \frac{2\eta - 3{\cdot}75}{(\eta - 1{\cdot}75)(\eta - 2)}\left\{\frac{Y}{1+Y} - 2(\eta - 1{\cdot}75)\right\} \\ \gamma &= \frac{50}{\eta^2}\,\frac{Y}{1+Y} \end{aligned}\right\} \qquad (9.13)$$

From these the position of the critical points is obtained and by solving the quadratic for ω the characteristic roots and their nature is determined. The table below summarizes the information obtained from this calculation.

In Fig. 6 is shown the position of these critical points in the phase plane, the value of k being inscribed by each marked point and the letter corresponding to the above table : all, of course, fall on the curve $\xi = \xi_s(\eta)$. In Fig. 7 the value of ω_1 and ω_2, the two characteristic roots, is shown and the letters on these curves show the parts of them which correspond to the stages in

Range of k	*Low temperature*		*Critical point*		*High temperature*	
	Nature	*Stability*			*Nature*	*Stability*
0	A	Node	Stable	M	Focus	Stable
0–0·34	AB	Node	Stable	LM	Focus	Stable
0·34 –0·847	BC	Focus	Stable	KL	Focus	Stable
0·847–3·33	CD	Focus	Stable	JK	Focus	Unstable
3·33 –3·64	DE	Node	Stable	IJ	Focus	Unstable
3·64 –4·5	EF	Node	Stable	HI	Node	Unstable
4·5 –5·90	FG	Node	Stable	GH	Saddle-point	Unstable
5·90			G Coalesence			

the above table. We may now inquire what this knowledge together with general topological considerations allows us to say about the phase plane as a whole.

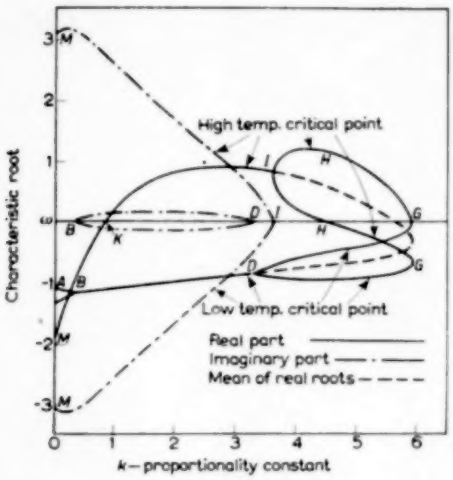

FIG. 7. Characteristic roots for varying k.

From earlier work there is some knowledge of the phase plane when $k = 0$. From the saddle-point there issue two trajectories which go to the stable critical points and from the boundary there arrive two trajectories which divide the phase plane into two parts, all trajectories in the one part going to the stable critical point there situated. When k increases beyond 0·34 and the low temperature point becomes a focus no significant change occurs for the trajectory from the saddle-point still proceeds there. But when k increases beyond 0·847 a radically different situation exists for then the high temperature singularity has become unstable and the trajectory leaving the saddle-point can certainly not arrive there. Three topological possibilities exist which would take care of this situation; these are shown in Fig. 8. Either the trajectory arriving at the saddle-point, B, now comes from the unstable critical point, C, and the trajectory leaving B, which formerly went to C, takes a detour around the bottom and goes to A, as is shown in Fig. 8 (i); or the two arms of the separatrix join together to form a closed loop and the trajectories within this loop tend outwards toward it while those without skirt it and go to A, as is shown in Fig. 8 (ii). Or a stable limit cycle, L, grows around C and attracts both the trajectory issuing from B and also all trajectories to the right of the separatrix, FBG. In the last case the division of the phase plane into halves is maintained, though the stable critical point of the right half is replaced by a stable limit cycle. In the second case all trajectories starting outside the closed loop will eventually arrive at A the low temperature state, while the loop itself forms a pseudo-limit cycle to which the trajectories from within tend, but since B is a critical point where $\dot{\xi}$ and $\dot{\eta}$ vanish the system will spend increasingly long periods in the neighbourhood of this point but never ceases to make excursions round the loop. In the first case, however, all trajectories, except the separatrices, tend to the one stable critical point A. It will later appear that the first alternative is what occurs but it is not possible to decide between them at this stage.

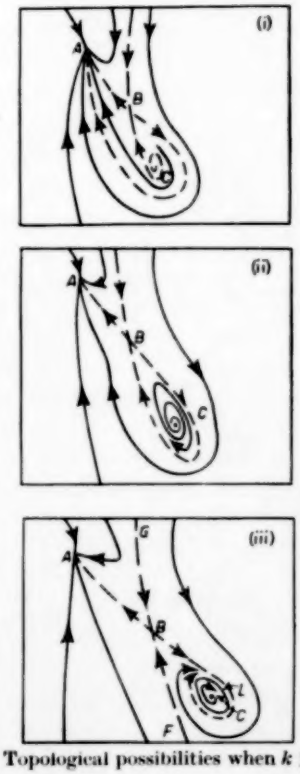

FIG. 8. Topological possibilities when $k > 0{\cdot}847$.

We do, however, know that as k increases through 4·5 the critical point C passes through the fixed point B and after this it is the moving critical point which is the saddle-point and the fixed point B which is an unstable node or focus. Moreover, one can determine the directions of the separatrices through the fixed saddle-point B, following the reasoning of par. 3, and they can be shown to vary only slightly. At $k = 4{\cdot}5$ the separatrices pass through $\xi = \frac{1}{2}$, $\eta = 2$ in the directions $d\xi/d\eta = -0{\cdot}5$ and $d\xi/d\eta = -0{\cdot}32$. If the third were the correct alternative of those presented in Fig. 8 the limit cycle would be forced to assume a very pointed vertex near $k = 4{\cdot}5$ and so a break-down into the form of (i) or (ii) would seem inevitable. But the alternative (ii) is unsatisfactory at this point also for a closed curve cannot be a trajectory without containing a critical point and if C is made to coincide with B it would leave the loop in (ii) without any critical point within it. The same objection cannot be raised against the configuration of Fig. 8 (i), however, for the closed loop when C coincides with B would here be not one trajectory, but two. Thus it already appears that (i) is the correct alternative, though the detailed calculation for confirmation will be determining. As k increases from 4·5 to 5·90 it is the saddle point which is now moving with the fixed unstable point within it, but this is basically the same configuration as before. At $k = 5{\cdot}90$, however, the node A and the saddle-point C coincide and that part of the loop going in anti-clockwise direction vanishes while the trajectory leaving the fixed unstable point B and going to the saddle-point C can no longer arrive there. Thus a limit cycle is left behind which is traversed in a clockwise sense and all trajectories from the still unstable point B wind outwards towards it. For values of k between 5·90 and 9, the reactor cannot but behave in a highly unsatisfactory manner, always ultimately tending to a regular cycle of temperature and concentration variation. Without full calculation nothing further can be said about the behaviour of this limit cycle save that as $k \to 9$ it can either close down on the fixed point $\xi = \frac{1}{2}$, $\eta = 2$ and vanish as this becomes stable or it can persist after $k = 9$. In the latter case an unstable limit cycle must grow up within it surrounding the now stable critical point. The method of the following paragraph enables us to decide which alternative is true.

10. THE TRANSITION AT $k = 9$

The study of the interesting phenomena which can occur when a critical point changes its stability was initiated by POINCARE [11] and is known generally in the texts on non-linear mechanics as "bifurcation theory". It goes essentially beyond what can be studied by the linearized equations though it is limited in that it can only say what takes place in the immediate neighbourhood of the change. It will, however, allow us to say which of the alternatives stated at the end of the previous paragraph is the correct one. The main ideas of the method will be first outlined, and then the details of the method given for the general case, and finally, the example being studied will be worked out.

Transition from instability to stability will normally take place when the real part of the characteristic roots ω of a focus turn from positive to negative. At the transition the roots are wholly imaginary and the solutions of the linearized equations give a system of concentric ellipses in the phase plane about the critical point. By a suitable linear transformation of co-ordinates these ellipses can be turned into circles, and the equations into an equation for r, the distance from the critical point in the transformed phase plane as a function of θ, the polar angle and the parameter k. This equation takes the form

$$\frac{dr}{d\theta} = R_1(\theta, k)\, r + R_2(\theta, k)\, r^2 + \dots \quad (10.1)$$

and for the transition value of k (say k^*), $R_1 \equiv 0$. This is to be expected, for the linearized equation, i.e., that obtained by neglecting R_2, etc., is to give a system of circles for which $dr/d\theta = 0$. If r_0 is the value of r when $\theta = 0$, an attempt is made to find a solution of the form

$$r = r(\theta, k) = r_0 u_1(\theta, k) + r_0^2 u_2(\theta, k) + \dots \quad (10.2)$$

by substituting and comparing the powers of r_0. This will represent a closed trajectory if after

the angle θ has increased by 2π the same value of r is obtained, i.e., if

$$r - r_0 = r_0\{u_1(2\pi, k) - 1\} + r_0^2 u_2(2\pi, k) + \ldots \quad (10.3)$$

is zero. Again at the transition value k^* the coefficient of r_0 must vanish and it is also found that $u_2(2\pi, k^*) = 0$. Expanding (10·3) as a Taylor series in powers of $(k - k^*)$ and retaining only the lowest order terms the condition for a limit cycle is

$$(k - k^*)\left[\frac{du_1(2\pi, k)}{dk}\right]_{k=k^*} + r_0^2 u_3(2\pi, k^*) = 0 \quad (10.4)$$

Thus when the first term is of the opposite sign to u_3 there are real values of r_0 different from zero which give limit cycles.

At a transition from instability to stability $[du_1/dk]_{k=k^*} < 0$ hence if $u_3 > 0$ limit cycles exist for $k > k^*$ and these must be unstable since they surround a stable critical point. If $u_3 < 0$ the limit cycles are stable surrounding the yet unstable critical point for $k < k^*$, and they disappear for $k > k^*$. It is in this way that the two alternatives may be distinguished.

To formulate this programme in more detail and in a way which is immediately applicable to our equations, the following equations are considered. Let $\lambda = k - k^*$ so that the transition of stability occurs at $\lambda = 0$, then the roots of the characteristic equation (3.10) are

$$\omega_{1,2}(\lambda) = \mu(\lambda) \pm i\,\nu(\lambda) \quad (10.5)$$

where
$$\mu(0) = 0 \quad (10.6)$$

Let the equations be

$$\dot{\xi} = \overline{P}(\xi, \eta) \equiv a(\lambda)(\xi - \xi_s) + b(\lambda)(\eta - \eta_s) + p^*(\xi, \eta) \quad (10.7)$$

$$\dot{\eta} = \overline{Q}(\xi, \eta) \equiv c(\lambda)(\xi - \xi_s) + d(\lambda)(\eta - \eta_s) + q^*(\xi, \eta) \quad (10.8)$$

and the local linearization about the steady state ξ_s, η_s is obtained by omitting the functions p^* and q^*. The characteristic equation of which the roots are (10.5) is thus

$$\omega^2 - \{a(\lambda) + d(\lambda)\}\,\omega + \{a(\lambda)\,d(\lambda) - b(\lambda)\,c(\lambda)\} = 0 \quad (10.9)$$

By making the substitution

$$\xi - \xi_s = 2(\mu - a)\,u + 2\nu\,v \quad (10.10)$$

$$\eta - \eta_s = -2\,c\,u \quad (10.11)$$

the canonical form of the equations (10.7) and (10.8) results

$$\dot{u} = \mu u - \nu v + p(u, v) \quad (10.12)$$

$$\dot{v} = \nu u + \mu v + q(u, v) \quad (10.13)$$

where $-2cp = -q^*(u, v)$ and

$$2\nu\,cq = cp^*(u, v) + (\mu - a)\,q^*(u, v) \quad (10.14)$$

These functions p and q contain the non-linear part of the equations and when expanded would contain only squares and higher powers of u and v. Though the formulae do not explicitly show it, it should be remembered that μ, ν, etc. are still functions of the parameter λ.

Now introduce polar co-ordinates in the u, v plane

$$u = r\cos\theta, \quad v = r\sin\theta \quad (10.15)$$

with the result that equations (10.12) and (10.13) become

$$r\frac{dr}{dt} = \mu(\lambda)\,r^2 + r\cos\theta\,p(r, \theta) + r\sin\theta\,q(r, \theta) \quad (10.16)$$

$$r^2\frac{d\theta}{dt} = \nu(\lambda)\,r^2 + r\cos\theta\,q(r, \theta) - r\sin\theta\,p(r, \theta) \quad (10.17)$$

and dividing one equation by the other

$$\frac{dr}{d\theta} = r\frac{\mu(\lambda)\,r + p\cos\theta + q\sin\theta}{\nu(\lambda)\,r + q\cos\theta - p\sin\theta} \quad (10.18)$$

this equation is expanded into the form

$$\frac{dr}{d\theta} = R_1(\theta, \lambda)\,r + R_2(\theta, \lambda)\,r^2 + R_3(\theta, \lambda)\,r^3 + \ldots \quad (10.19)$$

If

$$p(r, \theta) = r^2(p_{20}\cos^2\theta + p_{11}\cos\theta\sin\theta + p_{02}\sin^2\theta) + r^3(p_{30}\cos^3\theta + p_{21}\cos^2\theta\sin\theta + \ldots$$

and q is of similar form, then with $r_{ij} = \nu p_{ij} - \mu q_{ij}$ and $s_{ij} = \nu q_{ij} + \mu p_{ij}$,

$$R_1(\theta, \lambda) = \mu(\lambda)/\nu(\lambda) \quad (10.20)$$

$$R_2(\theta, \lambda) = \frac{1}{\nu^2}[r_{20}\cos^3\theta + (r_{11} + s_{20})\cos^2\theta\sin\theta + (r_{02} + s_{11})\cos\theta\sin^2\theta + s_{02}\sin^3\theta] \quad (10.21)$$

$$R_3(\theta, \lambda) = \frac{1}{\nu^2}[r_{30}\cos^4\theta + (r_{21} + s_{30})\cos^3\theta\sin\theta + (r_{12} + s_{21})\cos^2\theta\sin^2\theta + (r_{03} + s_{12})\cos\theta\sin^3\theta + s_{03}\sin^4\theta] \quad (10.22)$$

$$-\frac{1}{\nu}[q_{20}\cos^3\theta + (q_{11} - p_{20})\cos^2\theta\sin\theta + (q_{02} - p_{11})\cos\theta\sin^2\theta - p_{02}\sin^3\theta]\,R_2(\theta, \lambda)$$

If $r = r_0$, when $\theta = 0$, a solution may be formed

$$r(\theta, \lambda) = r_0\,u_1(\theta, \lambda) + r_0^2\,u_2(\theta, \lambda) + r_0^3\,u_3(\theta, \lambda) + \ldots \quad (10.23)$$

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and substituting and comparing coefficients of r_0 gives a series of recurrent differential equations

$$\frac{du_1}{d\theta} = u_1 R_1(\theta, \lambda) \tag{10.24}$$

$$\frac{du_2}{d\theta} = u_2 R_1(\theta, \lambda) + u_1^2 R_2(\theta, \lambda) \tag{10.25}$$

$$\frac{du_3}{d\theta} = u_3 R_1(\theta, \lambda) + 2 u_1 u_2 R_2(\theta, \lambda) + u_1^3 R_3(\theta, \lambda) \tag{10.26}$$

etc. By assumption $r = r_0$ when $\theta = 0$ so that $u_1 = 1$, $u_2 = u_3 = 0$ when $\theta = 0$. The solution to (10.24) is

$$u_1(\theta, \lambda) = \exp\left(\frac{\mu}{\nu}\theta\right) \tag{10.27}$$

and the solution of an equation of the form

$$\frac{du}{d\theta} = \frac{\mu}{\nu} u + f(\theta)$$

is

$$u(\theta) = \int_0^\theta \exp\frac{\mu}{\nu}(\theta - \phi) \cdot f(\phi)\, d\phi \tag{10.28}$$

If $r(2\pi, \lambda) = r_0$ it is necessary that

$$0 = \left\{\exp\left(2\pi\frac{\mu(\lambda)}{\nu(\lambda)}\right) - 1\right\} + u_2(2\pi, \lambda)\, r_0 + u_3(2\pi, \lambda)\, r_0^2 + \ldots \tag{10.29}$$

When $\lambda = 0$ this is clearly realized for the linearized equations for $\mu(\lambda) = 0$ and $\exp(2\pi\mu/\nu) - 1 = 0$. When so that $u_1 < 1$ it is observed that $u_2(2\pi, 0) = 0$, for using (10.28)

$$u_2(2\pi, 0) = \int_0^{2\pi} R_2(\phi)\, d\phi$$

and by (10.21) R_2 is an homogeneous polynomial of odd degree in $\cos\theta$ and $\sin\theta$ so that its integral from 0 to 2π vanishes. Again applying the formula (10.28) to the equation for u_3 and using (10.25)

$$u_3(2\pi, 0) = \left[u_2(2\pi, 0)\right]_0^{2\pi} + \int_0^{2\pi} R_3(\phi, 0)\, d\phi$$

and the first term on the right hand size is zero. From the well-known values of integrals of the form $\int_0^{2\pi} \cos^{2m}\phi \sin^{2n}\phi\, d\phi$ the value of $u_3(2\pi, 0)$ can be calculated from (10.22) in terms of the coefficients p_{ij} and q_{ij}.

If $\lambda \neq 0$, various zeros of (10.29) may be expanded as Taylor series in λ and this condition may be written as

$$0 = \lambda\left[2\pi\frac{\mu'(0)}{\nu(0)}\right] + \left[\frac{d}{d\lambda} u_2(2\pi, \lambda)\right]_{\lambda=0} \lambda r_0 + u_3(2\pi, 0)\, r_0^2 + \ldots$$

If this is to be satisfied the first and third terms must be equal and opposite, i.e. $\lambda = 0\ (r_0^2)$ and so $\lambda r_0 = 0\ (r_0^3)$ and the second term is negligible by comparison when λ is small. The size of the limit cycle for small λ is thus given by

$$r_0^2 = -\lambda 2\pi \frac{\mu'(0)}{\nu(0)\, u_3(2\pi, 0)} \tag{10.30}$$

If $\mu'(0) < 0$ the transition is from instability to stability. Then r_0 is real if either

(a) $u_3 > 0$, $\lambda > 0$; when an unstable limit cycle grows around the stable point, or

(b) $u_3 < 0$, $\lambda < 0$; when a stable limit cycle around the unstable point shrinks around it and vanishes as it becomes stable.

For $\mu'(0) > 0$ the transition is from stability to instability and either an unstable limit cycle shrinks on the critical point ($u_3 > 0$, $\lambda < 0$) or a stable limit cycle grows around the unstable point ($u_3 < 0$, $\lambda > 0$).

Applying this technique to our example gives $\lambda = k - 9$, $\mu = -\lambda/8$,

$$\nu = \sqrt{(\lambda + 4)(36 - \lambda)}/8 \tag{10.31}$$

$$2\pi\mu'(0)/\nu(0) = -\pi/6 < 0$$

$$u_3(2\pi, 0) = 78{\cdot}0707\ \pi > 0$$

and hence $$r_0 = 0{\cdot}0462\ \lambda^{1/2} \text{ for } \lambda > 0 \tag{10.32}$$

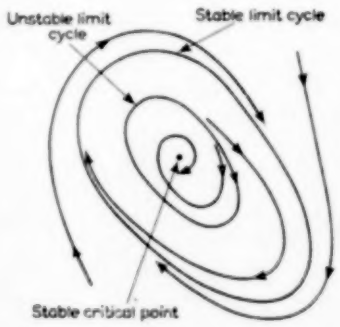

FIG. 9. The situation immediately after local control has been attained.

We thus arrive at the very important conclusion that the limit cycles do not vanish as k increases through 9 but rather that an unstable limit cycle around the controlled point within the remaining stable limit cycle. The situation in the phase plane for k slightly greater than 9 is thus as shown in Fig. 9. The circle of radius. r_0 transforms back

into an ellipse in the ξ, η plane within the nearly elliptical stable limit cycle. A trajectory starting from any point within the unstable limit cycle will spiral inwards to the controlled point but any other initial point will give a trajectory which tends to wrap itself around the stable limit cycle. Thus control has really only been achieved over the interior of the unstable limit cycle and a perturbation of the system which leads outside of this will result in the system performing the limit cycle. As k increases still further one might expect the stable limit cycle to shrink and the unstable limit cycle to grow until they coalesce and evaporate leaving one stable critical point in the phase plane and control has finally been established. This behaviour, however, cannot in general be fully decided without detailed calculation. It will be noted that all that has been required in the foregoing discussion is the expansion of the non-linear functions $\overline{P}(\xi, \eta)$ and $\overline{Q}(\xi, \eta)$ as far as the third-order terms; this, though it involves a certain amount of algebraic labour, does not demand the machinery required by the full scale integration of the equations and is, moreover, a valuable preliminary to the latter.

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In a certain case, however, a little more can be said about the behaviour of the limit cycle when $k > 9$ and since this applies to the present example the description of results, which follows in the next paragraph, will be anticipated to explain this. Supposing that at $\lambda = 0$ the stable limit cycle is already of very small size and has been decreasing for increasing negative λ, then it may be expected that the expanding unstable limit cycle will coincide with the stable one at some small value of $\lambda > 0$ and it should be possible to estimate this.

If the stable limit cycle is small it will be nearly elliptical and its form will satisfy the linearized differential equations. If it is given by the equation

$$f\,\xi^2 + 2\,g\,\xi\,\eta + h\,\eta^2 = 1 \qquad (10.33)$$

then substituting from the linearized equations the coefficients f, g, h must satisfy

$$\left.\begin{aligned} af + cg &= 0 \\ bf + (a+d)\,g + ch &= 0 \\ bg + dh &= 0 \end{aligned}\right\} \qquad (10.34)$$

and the condition for consistency is that the determinant of these equations should vanish, i.e. $(a + d)(ad - bc) = 0$. This is satisfied since $a + d = 2\mu = 0$ at a transition. The ellipse is thus

$$c\,\xi^2 + 2d\,\xi\,\eta - b\,\eta^2 = d/g \qquad (10.35)$$

The transformation (10.10), (10.11) is applied to this remembering that $a + d = 0$, $\nu^2 = ad - bc$ and it is found that it gives

$$u^2 + v^2 = d/4\,\nu^2\,cg = {r_0}^2$$

and the expression on the right hand side is just the square of the radius of the circular limit cycle in the u, v plane, i.e.

$$\frac{1}{{r_0}^2} = \frac{4\nu^2\,c}{d}\,g \qquad (10.36)$$

On the other hand, the reciprocals of the squares of the semi axes of the ellipse (10.35) are the roots of the quadratic

$$X^2 - X\,\frac{g}{d}(c - b) + \frac{g^2}{d^2}\,\nu^2 = 0$$

$$\text{i.e.} \qquad X = \frac{1}{2}\,\frac{g}{d}\left[(c - b) \mp \sqrt{(c - b)^2 - 4\,\nu^2}\right] \qquad (10.37)$$

If B is the semi-minor axis on eliminating g/d between (10.36) and (10.37)

$$B^2 = {r_0}^2\,8\,\nu^2\,c/\left[(c - b) + \sqrt{(c - b)^2 - 4\,\nu^2}\right] \qquad (10.38)$$

which gives an expression for the growth of B when r_0 is substituted from (10.32). In this case $B = 0{\cdot}052\,\lambda^{1/2}$.

Anticipating a little the results to be exhibited in the next paragraph and referring to Fig. 21, it is seen that as $k \to 9$, i.e. $\lambda \to 0$, the minor axis of the limit cycle becomes quite small and is rapidly decreasing. In fact when $k = 9$

$$\lambda = 0,\ B^* = 0{\cdot}026,\ dB^*/d\lambda = -0{\cdot}180$$

It is expected that the minor axis of the stable limit cycle for values of k near 9 will be approximately

$$B^* = 0{\cdot}026 - 0{\cdot}180\,\lambda$$

and when this equals $B = 0{\cdot}052\,\lambda^{1/2}$ both limit cycles will coincide and vanish. This gives a quadratic for $\lambda^{1/2}$ and from the positive root of this, $\lambda = 0{\cdot}025$.

Thus for as low a value as $k = 9{\cdot}025$ it is expected the limit cycles will disappear. It is perhaps regrettable that this state of partial control should have disappeared so soon in the particular example chosen, but there was no way of knowing this in advance. The importance of the phenomenon should not be overlooked for this reason, for in other cases it might be that the area over which control had really been obtained continued to be quite small long after the control parameter had passed through its critical value. Any imperfection of control, such as must certainly occur in practice, may be expected to increase the likelihood of this happening.

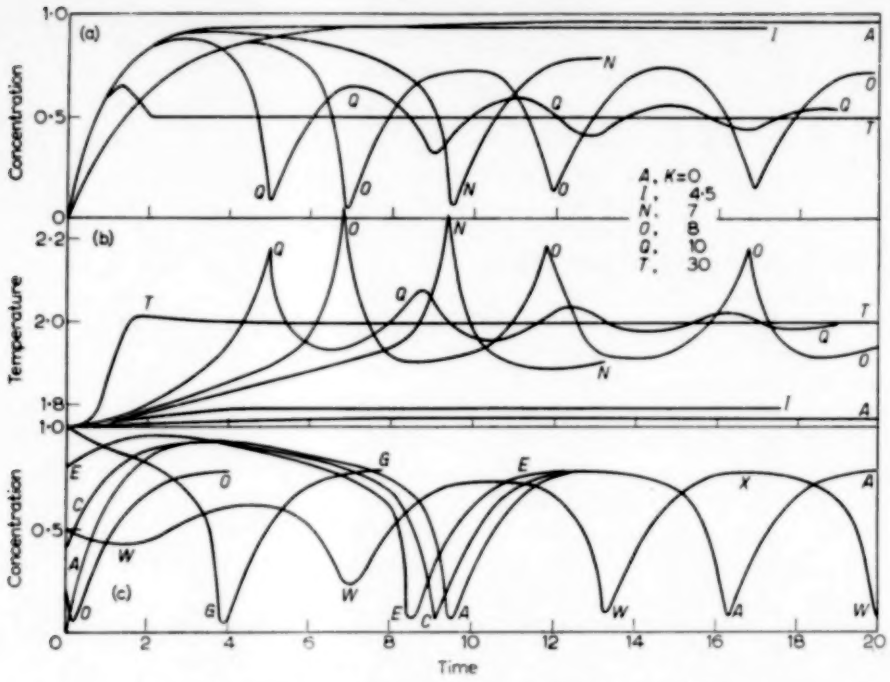

FIG. 10. Concentration and temperature as functions of time.

11. DESCRIPTION OF RESULTS

An account of the results of extensive calculations which have been done on the two equations (9.6) and (9.7) will now be given. This will give a complete picture of the evolution of control and show to what extent the predictions of the last two paragraphs have been valid. Those details of the calculation which are of general application will be discussed in the following paragraph; suffice it to say here that the curves of Figs. 10–21 are based on a numerical integration of the two equations. These calculations were performed on the Model 1103 of Remington-Rand Univac.

The region of the phase plane which is of interest is for $0 \leqslant \xi \leqslant 1$ (i.e. concentration, between 0 and 100 per cent of inlet value) and $1{\cdot}75 \leqslant \eta \leqslant 2{\cdot}45$ (i.e. temperatures between 300 and 580°K). This region is presented in Figs. 11–20 and to clarify the way in which the concentration and temperature depend on time a number of the trajectories are so plotted in Fig. 10.

The phase plane when $k = 0$, shown in Fig. 11, has already been the subject of comment in par. 8 and it is in any case entirely similar to that found earlier by AMUNDSON and BILOUS [2]. The trajectory DA going from the bottom left hand corner to the low temperature critical point A is shown as a function of time in Fig. 10 (a) and (b) as the curves labelled A there. The curves in the top right hand corner of Fig. 11 which cross the high temperature border (such as that at E) will go to a high value of η and low value of ξ before making a sharp turn and coming back beneath the separatrix BC to the high temperature steady state C. From a practical point of view an extreme departure of temperature could probably not be tolerated and shows how inadvisable it would be to start the reactor full of the reactant mixture at inlet composition.

Fig. 12 shows the phase plane for $k = 0{\cdot}847$ very shortly before the critical point C becomes unstable. It shows little change from Fig. 11 except in the neighbourhood of the critical point C. The approach to C is very, very slow the last point of the trajectory as plotted, namely D, was reached in time $\tau = 4$. The trajectory

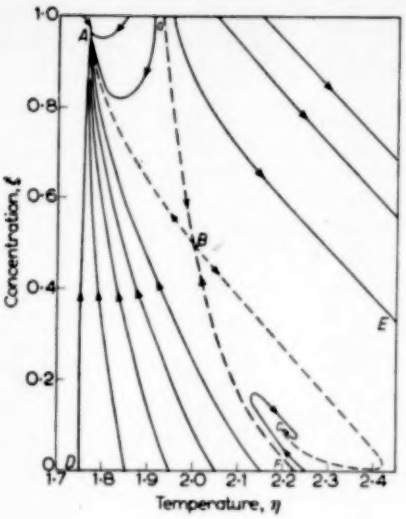

FIG. 11. Phase plane, $k = 0$.

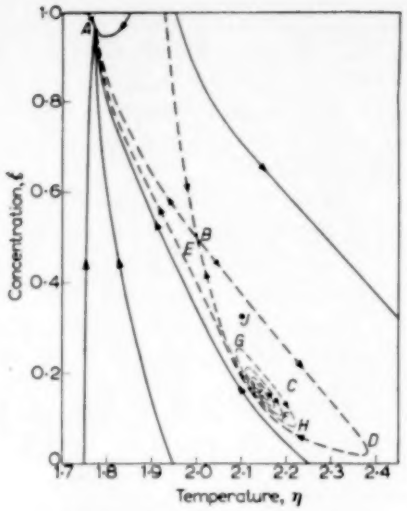

FIG. 13. Phase plane, $k = 1$.

was, however, computed long beyond this to $\tau = 249$ and this point is shown ***E***, still not too near ***C***. The arm ***FB*** of the separatrix has also moved over to higher temperatures. At $k = 1$ (Fig. 13), the critical point ***C*** is definitely unstable and the trajectory ***FGHB*** shown there winds outwards from ***C*** to ***B***. The other arm of the separatrix ***BDEA*** sweeps around very close to the arm ***BHGF*** but goes up to the stable critical point ***A***. Thus the calculations definitely establish that the alternative (i) of Fig. 8, which was thought probable on topological grounds, does in fact obtain. A trajectory from any point such as ***J*** within the loop will run down to a corner near ***D*** and then proceed to ***A*** passing through the very narrow strait between the curves ***HB*** and ***DE***.

The change from $k = 1$ to $k = 2$, i.e. between

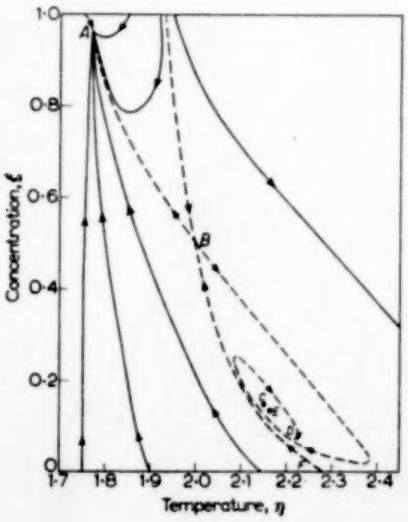

FIG. 12. Phase plane $k = 0{\cdot}847$.

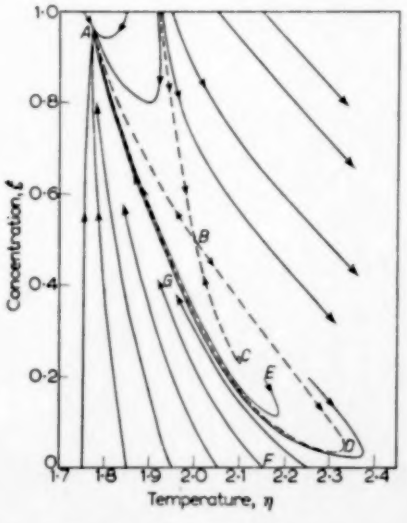

FIG. 14. Phase plane, $k = 2$.

Figs. 13 and 14, is comparatively slight and entirely as has been predicted. The unstable critical point C has moved toward B and its instability has become much more obvious. The arm of the separatrix BDA still has the same form and the trajectory EA is typical of those starting within the loop. Attention may be called here to the fact that not all trajectories have been drawn in full. This is not necessary and saves cluttering up the figures, particularly later ones. It is clear, for example, that the trajectory FG ultimately goes to A on a smooth and obvious course.

In Fig. 15, $k = 4{\cdot}5$, at which value the moving point C coincides with B, and the limb BC of the separatrix vanishes. All trajectories go to the stable point A and one such from inside the loop is shown, DA. The curves labelled I in Fig. 10 (a) and (b) are time plots for the trajectory EA of Fig. 15. With $k > 4{\cdot}5$ but $< 5{\cdot}9$ the appearance of the phase plane is similar to Fig. 14 save that B ($\xi = \frac{1}{2}$, $\eta = 2$) is now the unstable node and C, between B and A, is the saddle-point. At approximately $k = 5{\cdot}9$ A and C coalesce and leave behind a stable limit cycle. Fig. 16 shows the phase plane for $k = 6$ just after this limit cycle has evolved; note that its top end is still very sharp, according with the fact that it is formed from a curve with a cusp there. Trajectories from all points outside wind themselves around it, while such a one as DEF starting from a point within winds outwards and very quickly takes up the form of the limit cycle.

The way in which a limit cycle gets into its stride may be seen from the curves of Fig. 10 (c). These all apply to the case $k = 7$, for which a phase plane diagram is not given but whose limit cycle can be seen in Fig. 21. The letters by the curves denote the initial point of the trajectory according to the following scheme:

A, $\xi = 0$, $\eta = 1{\cdot}75$	G, $\xi = 1{\cdot}0$, $\eta = 1{\cdot}85$
C, $\xi = 0{\cdot}4$, $\eta = 1{\cdot}75$	O, $\xi = 0{\cdot}2$, $\eta = 2{\cdot}25$
E, $\xi = 0{\cdot}8$, $\eta = 1{\cdot}75$	W, $\xi = 0{\cdot}5$, $\eta = 2{\cdot}01$

The fully developed limit cycle is the arc WXW to the right of the figure which the trajectory W starting from within picks up very quickly. Although, as Fig. 21 shows, the part of the limit cycle with greatest ξ is rather pointed when ξ is plotted against τ this part is a flat hump. This is because the limit cycle is traversed very slowly at this low temperature, high concentration part whereas at the high temperature end the movement is very rapid and produces the sharp, almost cusped, dip near the W's of Fig. 10 (c). It is clear that all the other curves are going to tend towards the same form, though since they start from widely different parts of the phase

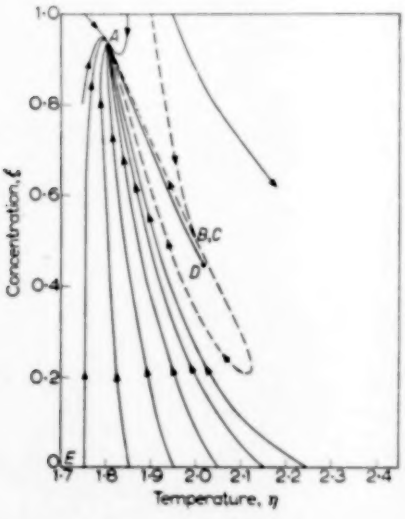

FIG. 15. Phase plane, $k = 4{\cdot}5$.

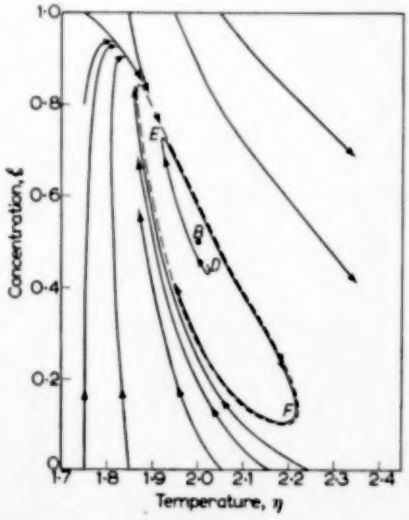

FIG. 16. Phase plane, $k = 6$.

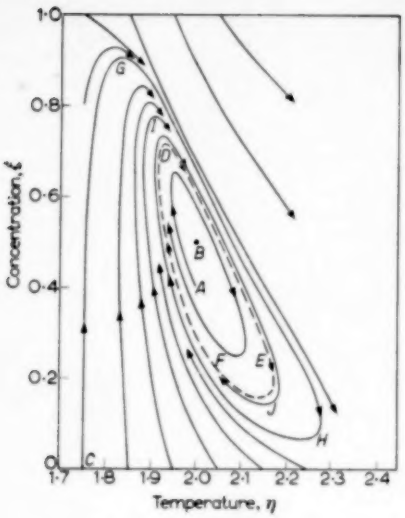

FIG. 17. Phase plane, $k = 8$.

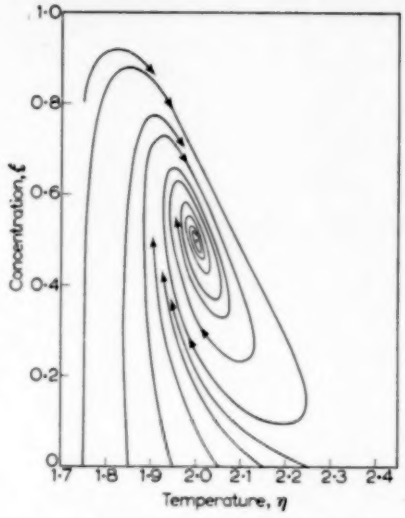

FIG. 19. Phase plane, $k = 10$.

plane there is a phase lag between them, which shows up as a displacement of the ultimate form of curve in the τ direction.

Fig. 17, the phase plane for $k = 8$ shows the development of the limit cycle. The curve O of Figs. 10 (a) and (b) shows ξ and η plotted separately against τ for the particular trajectory *CGHIJ*. A closer study of the development of the limit cycle is given in Fig. 21, from which its decrease in size and tendency to become more elliptical as $k \to 9$ is evident. The inset shows the way in which the periodic time, T, of the limit cycle and also its least semi-diameter, B, vary as functions of k. It is seen that though the size of the limit cycles falls rapidly to zero as $k \to 9$ the periodic time T tends to a limit of approximately 4. This is because the limit cycle is closing down on a critical point at which the

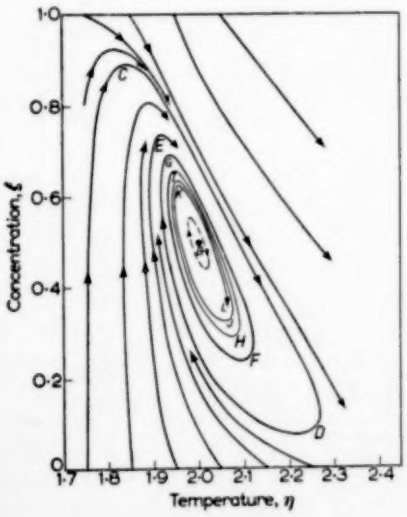

FIG. 18. Phase plane, $k = 9$.

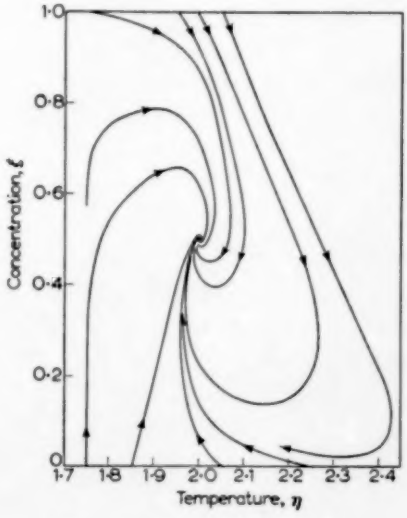

FIG. 20. Phase plane, $k = 30$.

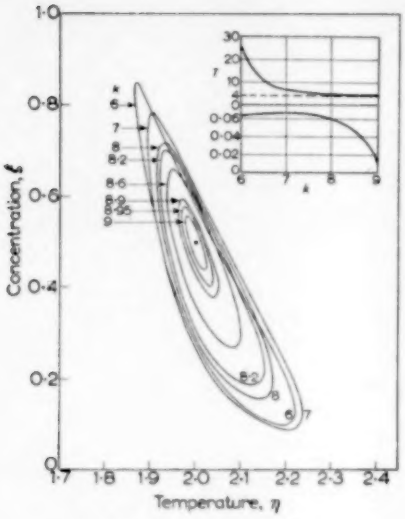

FIG. 21. Limit cycles.

velocity vanishes; though the perimeter is decreasing, the periodic time, which is approximately the quotient of the perimeter and velocity, tends to a non-zero limit.

The situation, $k = 9$, is shown in Fig. 18. Within the stable limit cycle the tendency of a trajectory to spiral towards it is almost imperceptible and this region is virtually one where small oscillations will persist. Even from outside the approach is extremely slow as is shown by the trajectory *CDEFGHIJKL*, which even after five oscillations is far from the limit cycle. This is wholly in keeping with the picture formed from the calculations of the preceding paragraph, where it was seen that for as low a value of k as 9·025 the limit cycle system would have vanished. Extensive calculations for values of k just greater than 9 confirm this.

The way in which control of the whole phase plane is finally attained is seen in Figs. 19 and 20. In the former, for $k = 10$ a rather weak form of control obtains, and its takes a number of oscillations before the concentration and temperature settle down to their controlled values; the curves *Q* of Fig. 10 (a) and (b) show this. In the latter when $k = 30$ all trajectories spiral in to the controlled point and their oscillations are almost immediately negligible. This is confirmed by the curves *T* of Fig. 10 (a) and (b).

CONCLUSIONS

It has been shown how the heat transfer to a cooling system subject to control can be approximated by a quadratic expression in the reactor temperature. Using this approximation a simple system with a dominant first order reaction is set up for study by the topological methods of non-linear mechanics. The uncontrolled system has three steady states, two stable and a third unstable, of which the control is being studied. It is shown that as the control parameter is increased the steady states change both in position and stability, and that stable limit cycles can develop. This represents a particularly undesirable feature of reactor behaviour corresponding to a continuous cyclic variation of temperature and composition, which the reactor ultimately follows whatever its starting conditions. A more subtle difficulty arises just after local control of the steady state is attained, for this stable limit cycle, though small, does not disappear. Instead an unstable limit cycle is generated around the steady state and within the stable limit cycle. Thus, although the criteria of local stability assure control at the steady state, this control only extends to small disturbances which do not take the system outside the unstable limit cycle. This phenomenon emphasizes the importance of using the method of non-linear mechanics, without which it would go undetected. Moreover, the fact that it happens even with a perfect controller (though somewhat ephemerally in the particular example considered) suggests that it is still more likely with imperfect control.

LIST OF SYMBOLS

ΔH = Heat of reaction (2)
T = Temperature
$U = VU^*/q\sigma_0(-\Delta H)$ reduced h.t.f. (2)
V = Volume of reactor (2)
X, X_j = Chemical species (2 and 14)
Y = Abbreviation for the function

$$\exp\left\{50\left(\frac{1}{2}-\frac{1}{\eta}\right)\right\} \quad (9)$$

$d_e = 1 + \alpha + 1 + \beta - \gamma$ (3)
$d_f = (1 + \alpha)(1 + \beta) - \gamma$ (3)
k = Proportionality constant
q = Flow rate of reactants (2)
q_c = Flow rate of coolant (2)

t = Time (2)
P = Reduced reaction rate (2)
α, β, γ = Stability parameters (3)
$\eta = c\rho T/x_0(-\Delta H)$, reduced temperature (2)
$\eta_r = K^{-1} q_{cs}/q$, half range of temperature causing valve to move
$\xi = x/x_0$, reduced concentration (2)
$\lambda = (k - k^*)$ in paragraph 10
$\tau = qt/V$, reduced time (2)
ω = Roots of characteristic equation (3 and 6)

Suffixes and affixes

c = Coolant
0 = Initial value
s = Steady state value
$*$ = Deviation from steady state (4)
m = Maximum value

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Chemical Engineering Science 1958, Vol. 7, pp. 148 to 155. Pergamon Press Ltd.

An analysis of chemical reactor stability and control—III*

The principles of programming reactor calculations. Some extensions

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Abstract—The increasing use of automatic computers for chemical engineering calculations makes it desirable to give an outline of the programme used here. This is so constructed that it can be rapidly modified for many more difficult problems. To round off the question of proportional control with very high amplification the limiting form of off–on control is discussed. Finally the extension is given to simultaneous reactions in more than one reactor and the general conclusions of the problem are discussed.

Résumé—L'utilisation croissante des calculateurs automatiques dans les calculs de Génie chimique rend nécessaire de donner un aperçu du programme employé ici. Il est établi de façon à pouvoir être modifié pour les problèmes difficiles. Pour circonvenir la question du contrôle proportionnel avec une très grande amplification, les limites du contrôle " tout ou rien " sont précisées. Finalement les auteurs donnent l'extension de la méthode au cas des réactions simultanées prenant place dans plusieurs réacteurs et discutent les conclusions générales du problème.

Zusammenfassung—Die steigende Verwendung automatischer Rechner für verfahrenstechnische Berechnungen lässt es wünschenswert erscheinen, das hier verwendete Programm zu beschreiben. Dieses ist so gestaltet, dass es schnell für die verschiedensten Probleme abgeändert werden kann. Um die Frage der Proportionalregelung mit sehr hoher Verstärkung abzurunden, ist die Grenzform der Aus–Ein-Regelung behandelt. Schliesslich werden die Betrachtungen auf gleichzeitige Reaktionen in mehr als einem Reaktor ausgedehnt und die allgemeinen Folgerungen des Problems diskutiert.

12. THE PRINCIPLES OF PROGRAMMING THE CALCULATIONS

THE considerable amount of calculation which lies behind the results presented here was performed on the Univac Scientific Computer, Model 1103. This machine is well-suited, both in size and versatility, to this type of calculation, which would indeed have demanded an impossible amount of time and labour to do by hand. While much of the detail of the programme is particular to the machine used, and thus unsuitable to be described here, its overall strategy and general principles would apply to almost all modern high-speed computing devices and are the same for the more general problem treated later. In view of the increasing importance of automatic computers in this field we sketch the programme in such a form as to allow it to be adapted to any problem of performance or control of a continuous flow reactor.

To obtain the concentration temperature histories of the converter it is necessary to integrate the pair of equations (9.1) and (9.2) from a given initial state ξ_0, η_0 until such time as the future behaviour is predictable. This may be either because the system is very close to a steady state or because it is performing a limit cycle. The Runge–Kutta method of integrating non-linear simultaneous equations numerically is well-known (e.g. INCE [7]†) and has been adapted to machine use by GILL [6]. A finite interval $\Delta\tau$ is chosen and the corresponding increments

*For ease of reference the numbering of the sections and figures is continuous with Parts I and II.
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†All references are listed at the end of Part I of this paper (p. 131).

$\Delta\xi$ and $\Delta\eta$ are calculated from the equations in such a way that the error is proportional to $(\Delta\tau)^5$; since the number of steps in a trajectory is inversely proportional to $\Delta\tau$ the error in the whole trajectory is of the order of $(\Delta\tau)^4$.

As each point of the trajectory is obtained several tests are applied to decide whether (a) a monitoring signal should be printed out on the typewriter, (b) the calculated point should be permanently recorded or (c) the trajectory should be stopped.

The first class of test is merely a convenience to give the operator some idea of how the trajectory is shaping; it was arranged for a period to be printed for every 25 points of the trajectory and for the sign of $\dot{\eta}$ to be printed every time it changed. In general far more points are calculated than can possibly be used and since the recording of a number involves converting it to decimal and punching a tape, both relatively lengthy operations, it is uneconomical to record more than is necessary. When a point ξ_P, η_P had been punched out it was therefore arranged that no point would be recorded until $|\xi - \xi_P|$ or $|\eta - \eta_P|$ exceeded certain limits. Finally the stopping tests can be worked in with the preceding tests quite easily. If the number of points between each punch out is recorded then the growth of this number beyond a certain limit M denotes that the steps are so small that the movement is almost negligible and the trajectory is approaching a critical point. Again the change of sign of $\dot{\eta}$ from $+$ to $-$ denotes the fact that η has passed through its maximum value, i.e. the trajectory has turned a corner. If this maximum value is compared with the value of η the previous time that it passed through its maximum the difference will become very small as a limit cycle or focus is approached. The trajectory may be stopped therefore when this difference falls below a preassigned value. A trajectory is also stopped when it goes outside a prescribed region of the phase plane. In all cases the last point is recorded and a monitoring sign to show the type of stop is printed out. The details of these tests will be published elsewhere.

The programme is composed of a number of sub-routines and these are joined together in the scheme shown in Fig. 22. There are three routines which from given values of ξ and η will perform the necessary substitution in the equations:

A calculates $P\ (\xi,\ \eta)$ from a given kinetic expression,
B calculates $\dot{\xi}$ from equation (9.1),
C calculates $\dot{\eta}$ from equation (9.2).

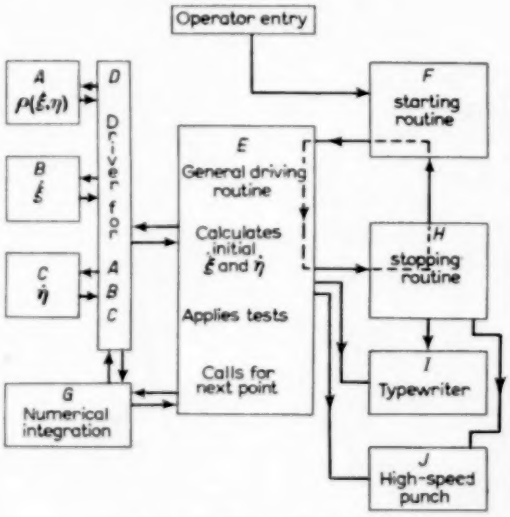

FIG. 22. The programme.

These three are organized by a driver sub-routine *D*, which calls for them in the correct order. The core of the programme is the general driving routine *E*, which calls for the calculation of $\dot{\xi}$ and $\dot{\eta}$ and then for the next point of the trajectory to be calculated by the sub-routine *G*; *G* is the sub-routine for carrying out GILL's adaptation of the Runge–Kutta method, in the course of which it calls on *D* for other values of the derivatives. The general driving routine *E* also applies the various tests described above and accordingly instructs the following sub-routines:

H, the stopping routine arranges the necessary print out and then calls for the next trajectory,

I, the typewriter routine prints out the monitoring symbols and the indication of the type of stop,

J, the punch-out routine, which converts the given point to decimal and punches a tape.

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Finally there is a routine F which is called for at the beginning of each trajectory either by the operator or by the stopping routine H. This deals with the setting up of certain registers to standard values and inserting the initial point of the trajectory. Fig. 22 shows the interrelation of these ; FEH is the main loop of the control which is traversed for every trajectory.

This scheme has been given in some detail for it will apply to most types of computer and its reduction to these basic units of organization allows the following generalizations to be made. If the kinetic equation of the reaction is changed it is only necessary to alter the sub-routine A. If in the equations one of the quantities which has been taken as constant (e.g. q) is made time dependent this only calls for a further sub-routine to calculate it and a slight modification of D to organize it in relation to B and C. If more than one reaction or reactor is considered further sub-routines for calculating the derivatives must be constructed and D modified to organize them. The sub-routine G can be written for any number of simultaneous first order equations so that no extra difficulty is introduced here, the tests used in E will, however, require to be made more general.

Finally from an economic standpoint the use of a large scale computer is easily justified. One trajectory involved 1320 steps and took 200 sec including the punching out of some 260 points. A skilled human computer working fast might perhaps get 6·6 steps done in 1 hr, i.e. take 3600 times longer. Machine time rented at \$360/hr is thus equivalent to human beings at 10 c/hr.

13. OFF–ON CONTROL

In par. 7 it was seen that as the gain k was increased, the range of temperature over which the flow rate was controlled decreased to zero, so that in the limit we had an off–on control. The equations in this case may be written

$$\dot{\xi} = 1 - \xi - P(\xi, \eta) \tag{13.1}$$

$$\dot{\eta} = \eta_0 - \eta - P(\xi, \eta) + k(\eta_c - \eta) \tag{13.2}$$

where

$$k = \begin{cases} 0 & \eta < \eta_s \\ k_1 & \eta = \eta_s \\ k_2 & \eta > \eta_s \end{cases} \tag{13.3}$$

If ξ_s, η_s is to be a steady state, k_1 must be such that

$$\eta_0 - \eta_s - P(\xi_s, \eta_s) + k_1(\eta_c - \eta_s) = 0 \tag{13.4}$$

Further, if the phase plane diagram for $k = k_1$ is drawn it is both necessary and sufficient that the half plane $\eta \geqslant \eta_s$ should contain no stable critical point for then any trajectory from this part of the plane will cross the line $\eta = \eta_s$ towards lower temperatures. But since the behaviour of the system for $\eta < \eta_s$ is represented by the phase plane for $k = 0$ it is again necessary and sufficient that this should contain no stable critical points for $\eta \leqslant \eta_s$.

Solving $\dot{\xi} = 0$ for $\xi = \xi_s(\eta)$ and substituting in $\dot{\eta} = 0$

$$(1 + k)\,\eta - \eta_0 - k\,\eta_c = P(\xi_s(\eta), \eta) = f(\eta), \text{ say,} \tag{13.5}$$

of which the right hand side is a sigmoid curve as shown in Fig. 23. The left hand side gives three straight lines for the three values of k, namely :

for $k = 0$ a line (A) of slope 1 passing through η_0;
for $k = k_1$ a line (B) of slope $1 + k_1$ passing through $\eta_3 = (\eta_0 + k_1\,\eta_c)/(1 + k_1)$;
for $k = k_2$ a line (C) of slope $1 + k_2$ passing through $\eta_1 = (\eta_0 + k_2\,\eta_c)/(1 + k_2)$

Consider also the lines : D, that tangent to the curve F of slope 1 whose point of tangency is of least η, and E, the tangent to F of slope

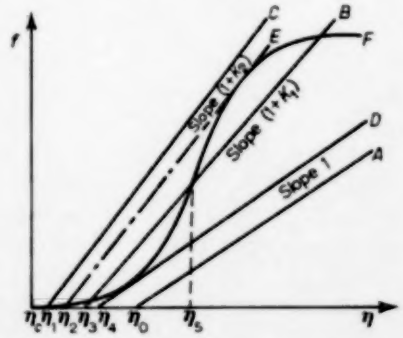

FIG. 23. Off–on control.

$1 + k_2$ with greatest value of η at tangency. Let these intersect the axis $f = 0$ at η_4 and η_2, respectively. Then provided $\eta_0 > \eta_4$ the line A must intersect F once only and that at a temperature greater than η_s. The line B intersects F at the point $\eta = \eta_s$, and again providing $\eta_1 < \eta_2$ the line C will intersect F only at a temperature lower than η_s. These three conditions provide sufficient restrictions on the disposable parameters to ensure only one steady state in the phase plane. They are

$$(\eta_s - \eta_0) + k_1(\eta_s - \eta_c) = f(\eta_s)$$
$$\eta_0 > \eta_4 \qquad (13.6)$$
$$\eta_0 + k_2\,\eta_c < (1 + k_2)\,\eta_2$$

Since k_2 will generally be fixed by the limit of flow the last condition gives an upper bound for η_c, the coolant temperature and the second a lower bound for η_0, the inlet reactant temperature. It is clear from the geometry of Fig. 23 that while these are sufficient they are not always necessary. Off-on control has been treated as the limiting case; in practice it would be a chattering type of control which would be unpleasant but the conditions (13.6) may be applied to the function U to insure stability even with the highest gains.

14. The Equations for Many Reactions and Reactors

Finally the most general situation with a chain of stirred tank reactors will be discussed with the intent to show what equations need to be set up to describe the behaviour of the system. As has been remarked the general principles of this analysis apply to the general situation and some features, such as the programming of the calculation, require only trivial modifications. The phase plane presentation is, of course, lost as soon as more than two variables are considered and the corresponding representations in space of higher dimensions requires a little more imagination.

Consider first the situation when the inlet concentrations, temperature and flow rate are time dependent. A mass balance for each substance gives the equations derived in par. 2,

$$V\frac{dx}{dt} = q(x_0 - x) - VR \qquad (14.1)$$

$$V\frac{dx_i}{dt} = q(x_{i0} - x_i) + VA_iR \qquad (14.2)$$

It would still be possible to eliminate all the concentrations except one, namely x. For multiplying (14.1) by A_i and adding the two equations gives an immediately integrable first order equation

$$x_{i0}(t) - x_i(t) = -A_i(x_0(t) - x(t)) + e^{-\int_0^t q/V\,d\tau}\int_0^t \frac{(q\tau)}{V}\left\{A_i\overline{x_0(t) - x_0(\tau)} + \overline{x_{i0}(t) - x_{i0}(\tau)}\right\}\left(\exp\int_0^\tau q/V d\tau\right)d\tau \qquad (14.3)$$

the necessary modification of the relation (2.2) to which it reduces if $x_0(t)$ and $x_{i0}(t)$ are constants. In this case the variation in flow rate is accommodated by taking $\tau = \int_0^t q(t')\,dt'/V$ though the reaction rate P then becomes time dependent. The elimination given by (14.3) is unprofitable from a practical point of view, for this formula would in any case be computed by a process equivalent to the integration of the differential equation. However because the elimination is possible there are essentially only three variables, one concentration, the temperature and the time. After a reduction to dimensionless concentration and temperature analogous to that of par. 2, there are two equations of the form

$$\frac{d\xi}{d\tau} = \overline{P}(\xi, \eta, \tau), \quad \frac{d\eta}{d\tau} = \overline{Q}(\xi, \eta, \tau)$$

These could be written in a more symmetrical form by the device of replacing τ on the right hand side of the equations by a dependent variable ζ, and adding a further equation $\zeta = \tau$ or $\frac{d\zeta}{d\tau} = 1$. Then, using the dot notation for $d/d\tau$

$$\dot{\xi} = \overline{P}(\xi, \eta, \zeta), \quad \dot{\eta} = \overline{Q}(\xi, \eta, \zeta), \quad \dot{\zeta} = \overline{R}(\xi, \eta, \zeta)$$

where of course $\overline{R} \equiv 1$. The behaviour of the reactor is thus represented in a three-dimensional space, through any point of which one trajectory passes. A projection of these trajectories on the ξ, η plane will retain some similarity to the time-independent phase plane, but these projections will intersect at many points besides the critical points. If the time dependent quantities tend ultimately to steady values then the trajectories will all be asymptotic to lines parallel to the ζ axis through the critical points of the phase plane which correspond to these steady values. In particular, if trajectories are taken backwards from the points of the ultimate separatrix they will intersect the plane $\zeta = \tau = 0$ in a curve, which will separate the regions that are attracted to one or other of the steady states.

It will now be shown that when m independent reactions are taking place simultaneously in a stirred-tank reactor, the m mass balances and the heat balance are sufficient to describe the system. Let the number of chemical species

taking part be n ($\geqslant m$) and denote these by $X_j, j = 1, 2, \ldots n$. If the stoicheiometric coefficient of X_j in the ith reaction is A_{ij}, the equation for that reaction may be written $\sum_{j=1}^{n} A_{ij} X_j = 0$. Since the reactions are assumed to be independent there is no linear combination which expresses any one of them in terms of the others and the species may be reordered so that the first m equations must include at least one of $X_1, \ldots X_m$. With this reordering of species the equations may then be reordered so that no $A_{ii} = 0$, $i = 1, \ldots m$. The equations retain their meaning when divided by a constant so let the ith equation be divided by A_{ii} and write $a_{ij} = A_{ij}/A_{ii}$ (i.e. $a_{ii} = 1$). The equations may now be written in a standard form $\sum_{j=1}^{n} a_{ij} X_{ij} = 0$, $i = 1, \ldots m$, or using the matrix notation

$$\mathcal{A} \cdot X = \left[\begin{array}{cccc:ccc} 1 & a_{12} & \cdots & a_{1m} & a_{1\,m+1} & \cdots & a_{1n} \\ a_{21} & 1 & \cdots & a_{2m} & a_{2\,m+1} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ a_{m1} & a_{m2} & \cdots & 1 & a_{m\,m+1} & \cdots & a_{mn} \end{array}\right] \left[\begin{array}{c} X_1 \\ X_2 \\ \cdot \\ \cdot \\ X_n \end{array}\right] = \left[A, B\right] X = 0 \qquad (14.4)$$

$\mathcal{A}$ is the $m \times n$ matrix of stoicheiometric coefficients a_{ij} and A is the leading square $m \times m$ submatrix, which by arrangement is non-singular and has units along the diagonal.

If N_i moles/unit volume of X_i are formed in the ith reaction then by the stoicheiometry of this reaction $a_{ij} N_i$ moles of X_j are formed and hence the total number of moles of X_j formed in all reactions is $\sum_{i=1}^{m} a_{ij} N_i$. Let x_i and x_{i0} be the instantaneous and initial concentrations (moles/unit volume) of X_i and write

$$\mathbf{x} = \left[\begin{array}{c} \mathbf{y} \\ \cdots \\ \mathbf{z} \end{array}\right] = \left[\begin{array}{c} x_1 - x_{10} \\ \cdot \quad \cdot \\ \cdots\cdots \\ \cdot \quad \cdot \\ x_m - x_{m0} \\ \cdots\cdots\cdots \\ x_{m+1} - x_{m+1,0} \\ \cdot \quad \cdot \\ \cdots\cdots \\ \cdot \quad \cdot \\ x_n - x_{n0} \end{array}\right] \text{ and } N = \left[\begin{array}{c} N_1 \\ \cdot \\ \cdot \\ N_m \end{array}\right]$$

Then clearly $x_j = x_{j0} = \sum_{i=1}^{m} a_{ij} N_i$ or in matrix notation $\mathbf{x} = \mathcal{A}' N$, where a prime denotes the transpose of $\mathcal{A}$. Using the partitioned form of $\mathcal{A}$ and x

$$\left.\begin{aligned} \mathbf{y} &= A' N \\ \mathbf{z} &= B' N \end{aligned}\right\} \qquad (14.5)$$

Since A is non-singular we can find N in terms of $\mathbf{y}$ and subsitute in the equation for $\mathbf{z}$ obtaining

$$\mathbf{z} = B' A'^{-1} \mathbf{y} \qquad (14.6)$$

This expresses the concentrations of $X_{m+1} \ldots X_n$ as a linear combination of those of $X_1, \ldots X_m$.

If $(dx_j/dt)_i$ denotes the rate of change of concentration of X_j due to the ith reaction alone, the rate of this reaction can be uniquely defined by a rate equation of the form

$$\frac{1}{a_{ij}} \left(\frac{dx_j}{dt}\right)_i = R_i(T, x_1, \ldots x_n) = R_i(T, x_1, \ldots x_m) \qquad (14.7)$$
$$i = 1, \ldots m$$

A matter balance for X_j gives

$$\frac{dx_j}{dt} = -\frac{q}{V}(x_j - x_{j0}) + \Sigma a_{ij} R_i, \; j = 1, \ldots n \qquad (14.8)$$

or in matrix notation

$$\frac{d\mathbf{x}}{dt} = -\frac{q}{V}\mathbf{x} + \mathcal{A}' R$$

It is now claimed that only first m of these equations are independent for one may write

$$\frac{d\mathbf{y}}{dt} = -\frac{q}{V}\mathbf{y} + A'R \qquad (14.9)$$

$$\frac{d\mathbf{z}}{dt} = -\frac{q}{V}\mathbf{z} + B'R \qquad (14.10)$$

Then substituting from (14.6) into (14.10)

$$\left(\frac{d}{dt} + \frac{q}{V}\right) B' A'^{-1} \mathbf{y} - B'R$$

$$= B' A'^{-1} \left[\left(\frac{d}{dt} + \frac{q}{V}\right)\mathbf{y} - A'R\right] = 0$$

and this equation is identically satisfied in virtue of (14.9).

If q and x_{j0} are functions of time one may multiply (14.9) by $B' A'^{-1}$ and subtract (14.10). Then

$$\left(\frac{d}{dt} + \frac{q}{V}\right)\mathbf{z} = \left(\frac{d}{dt} + \frac{q}{V}\right)(B' A'^{-1}\mathbf{y})$$

may be integrated to give $\mathbf{z}$ in a form similar to (14.3). Again, however, this is only necessary from a theoretical point of view to establish the dependence of the last $(n - m)$ equations on the first m, for computation all n equations would be used.

If h_i is the heat released in the ith reaction by the formation of one mole of X_i then a heat balance gives

$$Vc\rho \frac{dT}{dt} = qc\rho(T_0 - T) + V \sum_{i-1}^{m} h_i R_i - U^* V \qquad (14.11)$$

where U^* is the rate of heat removal by the cooling system. A reduction to dimensionless concentrations,

ξ_j, and temperature, η, may be effected entirely similar to that of par. 2 and obtain

$$\left.\begin{aligned}\frac{d\xi_j}{d\tau} &= 1 - \xi_j + \sum_i a_{ij} P_i \\ \frac{d\eta}{d\tau} &= \eta_0 - \eta + \sum_i b_i P_i - U\end{aligned}\right\} \quad (14.12)$$

where the constants b_i are proportional to the heats of reaction h_i. If $\zeta' = \{\xi_1' \dots \xi_m', \eta\}$, $\zeta_0 = \{1, \dots 1, \eta_0 - U\}$ and $C = \begin{bmatrix} A' \\ b' \end{bmatrix}$, $P' = P'(\zeta) = \{P_1, \dots P_m\}$, the primes denoting transposition, then

$$\frac{d\zeta}{d\tau} + \zeta = \zeta_0 + CP \quad (14.13)$$

Though these equations are written in matrix notation it must not be thought that they are linear. In general P will be anything but linear in the variables ζ. The steady state values are again found by solving the non-linear equations $\zeta_0 - \zeta + CP = 0$. If ζ_s is a solution of these and $\delta = \zeta - \zeta_s$ then

$$\frac{d\delta}{d\tau} = (D - I)\,\delta + 0(\delta^2) \quad (14.14)$$

where

$$D = C \cdot \operatorname{grad} P + u, \quad \operatorname{grad} P = \left[\frac{\partial P_i}{\partial \zeta_j}\right]$$

$$u = \begin{bmatrix} 0 & \dots & \dots & 0 \\ \cdot & & & \cdot \\ 0, \dots 0, & & & -\dfrac{\partial U}{\partial \eta} \end{bmatrix}$$

and $0(\delta^2)$ represents terms of the order of the squares of the differences $\zeta - \zeta_s$. The stability of the steady state is thus entirely defined by the latent roots of the matrix $D - I$. If one writes

$\alpha_{ij} = \left(\dfrac{\partial P_i}{\partial \xi_j}\right)_s$, general parameter corresponding to α of par. 3

$\beta = \left(\dfrac{\partial U}{\partial \eta}\right)_s$, the β of par. 3

$\gamma_i = \left(-\dfrac{\partial P_i}{\partial \eta}\right)_s$, the parameter corresponding to γ of par. 3

Then

$$(D - I) = C \begin{bmatrix} \alpha_{11}, \dots \alpha_{1m}, & -\gamma_1 \\ \cdot & \\ \cdot \dots & \\ \cdot & \\ \alpha_{m1}, \dots, \alpha_{mm}, & -\gamma_m \end{bmatrix} - \begin{bmatrix} 1, 0 \dots 0 \\ 0, 1, \dots 0 \\ \cdot \dots \\ \cdot \\ 0\,0 \dots 1 + \beta \end{bmatrix}$$

The stability of the steady state will thus depend on at most $(m^2 + m + 1)$ parameters. It is necessary now to find the conditions under which perfect proportional control on deviations of temperature will always succeed in locally stabilizing a steady state.

Perfect proportional control of the heat transfer function on signals of the deviation of temperature is equivalent to modifying the value of β. For if q_c is no longer a constant in the function $U(\eta, q_c, \eta_c)$ then

$$\beta = \frac{\partial U}{\partial \eta} = \left(\frac{\partial U}{\partial \eta}\right)_{q_c} + \left(\frac{\partial U}{\partial q_c}\right)\frac{dq_c}{d\eta}$$

and $dq_c/d\eta = k$, the control constant. If the latent roots of $(D - I)$ have negative real part local stability is assured. Let

$I - D = M + N$ where $M = I - C\,[\alpha_{ij} \vdots -\gamma_i]$

$$N = \begin{bmatrix} 0 \dots 0 \\ \cdot \quad \cdot \quad \cdot \\ 0 \dots \beta \end{bmatrix}$$

and denote the leading $m \times m$ submatrix of M by L. The expansion of $|\lambda I + M + N| = 0$ is an equation of the $(m + 1)$th degree in λ.

$$\lambda^{m+1} + \lambda^m sp_1(M + N) + \lambda^{m-1} sp_2(M + N) + \dots |M + N| = 0$$

where $sp_r A$ is the sum of all the diagonal submatrices of order $r \times r$ of a matrix A.

$$sp_{m+1}(M + N) = \det(M + N) = |M + N| = |M| + \beta|L|$$

Similarly

$$sp_1(M + N) = sp_1 M + \beta, \; sp_r(M + N) = sp_r M + \beta\, sp_{r-1} L$$

Writing the characteristic equation as

$$\lambda^{m+1} + a_1 \lambda^m + a_2 \lambda^{m-1} \dots a_{m+1} = 0$$

The Routh–Hurwitz criteria for roots of negative real part are

$$a_1 > 0, \begin{vmatrix} a_1 & 1 \\ a_3 & a_2 \end{vmatrix} > 0, \text{ etc.}$$

and from the rth criterion

$$\begin{vmatrix} a_1 & 1 & 0 & 0 & \cdot & \cdot & \cdot \\ a_3 & a_2 & a_1 & 1 & \cdot & \cdot & \cdot \\ a_5 & a_4 & a_3 & a_2 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & & & \cdot & a_r \end{vmatrix} > 0$$

there emerges β^r multiplied by a factor $(sp_1 L)(sp_2 L) \dots (sp_{r-1} L)$. This can be made to dominate the determinant and force it to become positive provided all the $sp_1 L \dots$

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$sp_m L$ are positive. This sufficient condition involves only the α_{ij} for

$$L \equiv (l_{ij}) = \begin{bmatrix} 1 & a_{21} & \cdots & a_{m1} \\ . & . & . & . \\ a_{1m} & a_{2m} & \cdots & 1 \end{bmatrix} \begin{bmatrix} \alpha_{11} & \cdots & \alpha_{1m} \\ . & . & . \\ \alpha_{m1} & . & \alpha_{mm} \end{bmatrix}$$

where $l_{ij} = \sum_{k=1}^{m} a_{ki}\,\alpha_{kj}$. It is interesting to note that the possibility of successful control depends only on the m^2 parameters α_{ij}, but the ease of control will depend largely on the further m parameters γ_i.

If r reactors are connected in series so that the product of one passes (perhaps after modification) to the next there will be a set of $(m + 1)$ equations for each reactor. In addition relations between the inlet concentrations and temperature of one reactor in terms of the exit conditions of the preceding one will exist. If an affix (k) denotes the value appropriate to the k^{th} reactor, a straight through connection with no heat loss between one reactor and the next simply gives $x_i^{(k+1)} = x_{i0}^{(k)}$, $T^{(k-1)} = T_0^{(k)}$. It will be supposed however that in general some of the flow is bypassed and the flow rate made up from some other stream. Let $\tilde{q}^{(k)}$ be the fraction of the flow $q^{(k)}$ out of the (k)th reactor which goes to the $(k + 1)$th and let an additional stream of flow rate $\hat{q}^{(k)}$ and composition $\hat{x}_i^{(k)}$ be introduced at this point. Then if mixing is complete

$$x_{i0}^{(k+1)} = (\tilde{q}^{(k)} x_i^{(k)} + \hat{q}^{(k)} \hat{x}_i^{(k)})/q^{(k+1)}$$

and

$$q^{(k+1)} = \hat{q}^{(k)} + \tilde{q}^{(k)}$$

If the concentrations x are reduced to dimensionless form ξ then

$$\xi_{i0}^{(k+1)} = \kappa^{(k)}\,\xi_i^{(k)} + \kappa\,(1 - \kappa^{(k)})\,\hat{\xi}_i^{(k)} \qquad (14.15)$$

and the $\kappa^{(k)} = 1$ for a direct connection. In a similar way the reduced temperatures will be connected by a relation of the form

$$\eta_0^{(k+1)} = \lambda^{(k)}\,\eta_i^{(k)} + (1 - \lambda^{(k)})\,\hat{\eta}^{(k)} - \mu^{(k)} \qquad (14.16)$$

where $\mu^{(k)}$ is a heat loss between the reactors.

These equations show that $r\,(m + 1)$ equations are necessary and sufficient to describe the behaviour of the chain of r reactors in which m reactions are simultaneously taking place. If however the inlet concentrations and temperatures are time dependent it is not wise to perform the possible eliminations but use the full set of $(2rn + r - n)$ equations of the form (14.12), (14.15) and (14.6).

CONCLUSIONS

An outline has been given of the strategy of the programme needed by a computer of the modern high speed type for calculating the transient behaviour of a continuous flow reactor. An important feature of economical programming is a flexible system of stopping tests, and one such is described. Simplifying assumptions have only been introduced for the purposes of exposition and the final paragraphs give the way in which certain extensions may be made. With very high amplifications of the controlling signal the controller meets the limits of its movement almost instantaneously and to ensure stability in the whole phase plane the necessary conditions for stable off–on control are discussed. Finally the method of extension of simultaneous reactions and many reactors is outlined, and it is shown that similar stability criteria can be established.

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LIST OF SYMBOLS

A_j = Stoicheiometric coefficients (2)
A_{ij} = Stoicheiometric coefficients (14)
$\mathcal{A}$ = Matrix of stoicheiometric coefficients (14)
A = Submatrix of $\mathcal{A}$ (14)
B = Submatrix of $\mathcal{A}$ (14)
C, D = Matrices (14)
D_s, D_1, D_2, D_3 = Regions of α, β, γ space (3)
$G(p)$ = Transfer function (5)
ΔH = Heat of reaction (2)
$I = \int_0^\infty |W(t)|^2\,dt$ (7)
K, K_1, K_2, K_3 = Proportionality constants (4)
L, M, N = Matrices (14)
$M(p)$ = Numerator of $G(p)$ (5)
$N(p)$ = Denominator of $G(p)$ (5)
N_i = Amount of X_i formed in i^{th} reaction (14)
N = Vector of N_i (14)
$\overline{P}, \overline{Q}$ = Abbreviation for r.h.s. of equations (3)
R = Reaction rate (2)
R_i = Reaction rate of ith reaction (14)
T = Temperature
U^* = Heat transfer function (2)
$U = VU^*/qx_0(-\Delta H)$ reduced h.t.f. (2)

V = Volume of reactor (2)
$W(t)$ = Response to unit disturbance (6)
X, X_j = Chemical species (2 and 14)
$\mathbf{X}$ = Vector of X_j (14)
Y = exp $\{50(\frac{1}{2} - 1/\eta)\}$ (9)
a_{ij} = A_{ij}/A_{ii} (14)
c = Specific heat (2)
d_e = $1 + \alpha + 1 + \beta - \gamma$ (3)
d_f = $(1 + \alpha)(1 + \beta) - \gamma$ (3)
h_i = Heats of reaction (14)
k = Proportionality constant
m = Number of reactions (14)
m_r = Coefficients in $M(p)$ (5)
n = Number of chemical species (14)
n_r = Coefficients in $N(p)$ (5)
p = Transform variable
q = Flow rate of reactants (2)
$\tilde{q}$ = Flow rate from one reactor to next (14)
$\hat{q}$ = Make up between reactors (14)
q_c = Flow rate of coolant (2)
r = Number of reactors (14)
t = Time (2)
x = Concentration of X (2 and 14)
$\mathbf{x}$ = Vector $(x_j - x_{j0})$ (14)
$\mathbf{y}, \mathbf{z}$ = Partitions of x (14)
Γ = Measure of control (6)
P = Reduced reaction rate (2)
P_i = Reduced reaction rate for ith reaction (14)
$\mathbf{P}$ = Vector of P_i (14)
α, β, γ = Stability parameters (3)
α_{ij}, γ_i = Generalized stability parameters (14)
δ = $(\partial U/\partial q_c)_s$ (14)
δ = $\zeta - \zeta_s$ (14)
ζ = Vector of ξ_j and η (14)
η = $c\rho T/x_0(-\Delta H)$, reduced temperature (2)
η_r = $K^{-1}q_{cs}/q$, half range of temperature causing valve to move
ξ = x/x_0, reduced concentration (2)
μ_i = Roots of $M(p)$
ν_i = Roots of $N(p)$
ρ = Density (2)
τ = qt/V, reduced time (2)
ω = Roots of characteristic equation (3 and 6)

Suffixes and affixes

c = Coolant
i = No. of reaction ($i = 1, \ldots m$)
j = No. of species ($j = 1, \ldots n$)
k = No. of reactor ($k = 1, \ldots r$)
o = Initial value
s = Steady state value
$*$ = Deviation from steady state (4)

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The flow-structure in packed beds

A theoretical investigation utilizing frequency response

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Abstract—A method is proposed whereby the flow structure of a system, or the physical structure of a packed bed or porous solid, may be analysed in terms of a model chosen (a) to approximate hydrodynamically to the system under investigation and (b) so that its effect on a flow of fluid containing a sinusoidally varying concentration of solute can be mathematically analysed.

The attenuation and phase angle of the output stream are measured for a number of different frequencies ; as many values of the frequency being chosen as there are values of the unknown variable to be found. From the measured results linear simultaneous equations are set up, which can be solved to give a histogram of the distribution of some desired parameter.

Results are given for models which illustrate the method and which are likely to be of use in practice.

Résumé—L'auteur propose une méthode qui permet d'analyser le mode d'écoulement d'un système, ou la structure physique d'un garnissage ou d'un solide poreux, en fonction d'un modèle choisi (a) pour avoir une bonne approximation hydrodynamique du système étudié et (b) pour analyser mathématiquement les effets produits sur l'écoulement d'un fluide contenant un soluté dont la concentration varie de façon sinusoïdale.

La diminution de l'amplitude et le déphasage du courant sortant sont mesurés pour diverses fréquences. On choisit autant de valeurs de fréquences qu'il y a de valeurs inconnues à trouver. Partant des résultats linéaires experimentaux, on établit des équations simultanées : équations qui peuvant être résolues pour donner la variation en fonction du temps de n'importe quel paramètre désiré.

Les résultats sont donnés pour des modèles qui illustrent la méthode et qui sont vraisemblablement utilisables dans la pratique.

Zusammenfassung—Um das Strömungsverhalten eines Systems oder die physikalische Struktur eines Festbettes oder eines porösen Körpers zu erforschen, wird die Verwendung eines Modells vorgeschlagen, mit dem man (a) das betrachtete System hydrodynamisch annähern kann und das es (b) möglich macht, sein Verhalten bei sinusförmiger Veränderung der Eintrittskonzentration analytisch vorauszuberechnen.

Die Verdünnung und der Phasenwinkel des austretenden Stromes werden für verschiedene Frequenzen gemessen und zwar werden ebenso viele Frequenzwerte gewählt wie Werte der unbekannten Variablen zu finden sind. Aus den Messergebnissen werden lineare simultane Gleichungen aufgestellt, deren Lösungen ein Spektrum der Verteilung eines gesuchten Parameters ergeben.

Zur Darstellung der Methode werden die Ergebnisse für Modelle mitgeteilt, die für den praktischen Gebrauch geeignet sind.

Introduction

In many systems, in the field of chemical engineering and in others, there is flow of fluid in which the bulk flow is made up of the sum of a number of individual flows, so that the " residence-time " of a small portion of the fluid may have any value between zero and infinity. A knowledge of this flow-structure, i.e. of the distribution of residence times, is often needed. For example, the flow-structure in a reactor is needed for the analysis of its behaviour and for its design.

Again, considering the system itself, e.g. a porous solid or packed bed, this is often treated as though it consisted of a collection of pores of

various lengths and diameters. To get a complete picture of this model it would be necessary to determine the frequency distributions of the lengths and of the radii of the pores. Instead, one has had to use an average value of the lengths of the pores (obtained by multiplying the length of the bed by a tortuosity factor), and an average value of the hydraulic radius m, obtained from

$$m = \epsilon/S,$$

where ϵ = porosity,

S = specific surface.

Even this average value is not of use when there is a wide spread in the distribution of pore diameters [1].

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In this paper methods are suggested whereby the frequency distributions of lengths and of diameters of the pores in a model which is considered to be the hydrodynamic equivalent of the packed bed or porous solid may be found experimentally.

In addition, the problem of residence times is considered for the special case where the fluid flow is considered to occur in a number of more or less identical channels; communicating with each channel are a number of stagnant pockets of fluid. The liquid in these pockets has infinite residence time but would play a part in any chemical or physical process by the diffusion of material into or out of them.

A method is suggested whereby the distribution (by volume) of pockets of different depths, and hence the amount of " dead " liquid relative to the total empty space in the system, may be found.

These are two examples of the type of information which might be required, and in the body of the paper will be developed briefly the mathematical equations which apply to these specific models. The same type of approach can be used for other models, the choice of which would have to be made after consideration of the actual system to be studied, and the procedure is summarized in the section headed Conclusion.

The problem is made up of two parts; the first is to determine residence times and the second is to relate this knowledge of residence times to the flow structure within, or the physical structure of, the system.

Danckwerts [2] has considered the use of step-functions and impulsive or "delta-functions" (Dirac) for the purpose of determining residence times but in this paper the use of " frequency response " will be considered because there are additional unknown variables in these problems, (each point on the distribution curve is an " unknown " which it is desired to find), and each additional value of the frequency used enables another equation to be set up.

In recent years a number of papers have appeared dealing with the application of frequency response to the analysis of flow systems. Thus Rosen and Winsche [3] have dealt with the theory of its application to chromatographic columns; Deisler and Wilhelm [4] with a theoretical and practical study of its application to a bed of porous solids; McHenry and Wilhelm [5] with its use in measuring mixing in a bed of spheres; Kramers and Alberda [6] with its application in continuous flow systems and Keyes [7] uses it in measuring radial mixing in turbulent flow in a tube.

To deal with the second part of the problem, viz. the relating of the residence times to the flow structure or physical structure of the system, the effect of any chosen model on a sinusoidally varying property must be calculated. Here this property will be the concentration of some solute, and the results for some models will be presented.

The Effect of the Models on the Phase and Amplitude-Modulation of the Concentration Wave

Model 1. *Channel with dead-spaces*

The structure is a channel or pore having a uniform cross-sectional shape and area; communicating with it are dead spaces or "pockets" distributed uniformly along the length of these channels. There is no flow in or out of these pockets and any transfer of solute in and out is by molecular diffusion only.

Here, then, the total volume occupied by fluid is made up of a part, in the channel, of which the residence time is finite, and part (the pockets), in which the residence time is

infinite. It is required to find the relative amounts of these two parts.

The method of attack is based on that of DEISLER and WILHELM. Fig. 1 shows a channel, distributed uniformly along which are pockets all of length l normal to the axis of the channel.

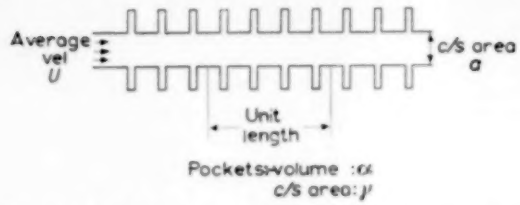

FIG. 1. Model 1 : a channel with distributed pockets of stagnant fluid.

The assumptions made are that :

The channel and all the pockets are full of the one fluid,
The pockets are of prismatic cross-section,
The concentration of solute is uniform across the channel,
The width of the pockets, in the direction in which z is measured, is small relative to the wavelength.

The "pockets", which have to be given geometric shape for the purpose of the analysis, mean in reality "dead-water" spaces in which there is no movement of liquid. The results of any calculations will therefore be in terms of the equivalent pockets.

At a distance z from the entrance to a channel, measured along its length, at time t, the equation of continuity for the dissolved solute is

$$D\frac{\partial^2 X_z}{\partial z^2} - \frac{U\,\partial X_z}{\partial z} - \frac{\partial X_z}{\partial t} - \beta\frac{\partial q}{\partial t} = 0, \qquad (1)$$

where D = longitudinal diffusivity, q = average concentration in the pocket (mass/volume), X_z = excess of concentration of solute at distance z over the time-average value for the system, U = average velocity in the channel, α = volume of pockets per unit length of channel, a = cross-sectional area of the channel and $\beta = \alpha/a$.

The solution to (1) is to be given by the real part of

$$X_z = A_z \exp\left[-i(\omega t - \phi_z)\right],$$

where ϕ_z = phase angle in the channel at distance z from the entrance. The general solution may be written

$$X_z = \overline{A}_z\, e^{-i\omega t}, \qquad (2)$$

where $\overline{A}_z$ is a complex amplitude.

In order to solve (1) explicitly it is necessary to obtain an expression for $\partial q/\partial t$, and this in turn requires that the differential equation

$$\frac{\partial X_{zy}}{\partial t} = \frac{D\partial^2 X_{zy}}{\partial y^2} \qquad (3)$$

should be solved for the pockets. (X_{zy} is the excess concentration of the solute at a distance y from the bottom of the pocket over the time-average value, and D is the molecular diffusivity of the solute.)

The solution to (3) will be of the form

$$X_{zy} = \overline{A}_z\, P \exp\left[-i(\omega t - \theta_y)\right], \qquad (4)$$

where the real part only is to be considered. θ_y is the phase-angle in the pocket at a distance y from the closed end, and P is an attenuation factor relating the amplitude in the channel at distance z to that in a pocket, at a distance y from the closed end, which is situated distance z from the entrance of the channel, as shown in Fig. 2.

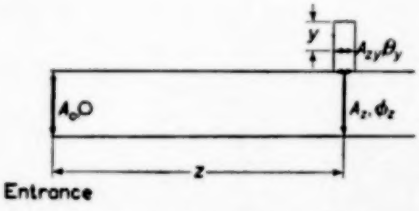

FIG. 2. The locations of amplitudes and phase-angles in a channel and a pocket.

Equation (3) is subject to the boundary conditions that at $y = l$, $X_{zy} = A_z \cos(\omega t - \phi_z)$ and at $y = 0$, $\partial X_{zy}/\partial y = 0$ (since there is no diffusion through the bottom of the pocket).

A solution to (3) obeying these boundary conditions is obtained by substituting

$$\theta_y = -\tan^{-1}\left\{\frac{\cosh\omega' l\cos\omega' l\sinh\omega' y\sin\omega' y}{\cosh\omega' y\cos\omega' y\cosh\omega' l\cos\omega' l} - \frac{\cosh\omega' y\cos\omega' y\sinh\omega' l\sin\omega' l}{+\sinh\omega' y\sin\omega' y\sin\omega' l\sinh\omega' l}\right\}$$

and $$P = \left(\frac{\cosh 2\omega' y + \cos 2\omega' y}{\cosh 2\omega' l + \cos 2\omega' l}\right)^{1/2}$$

into equation (4),

where $\omega' = \sqrt{\frac{\omega}{2D}}$.

Now $$\frac{\partial q}{\partial t} = \frac{D}{l}\left(\frac{\partial X_{zy}}{\partial y}\right)_{y=l},$$

and $\left(\frac{\partial X_{zy}}{\partial y}\right)_{y=l}$ may be obtained by differentiating (4).

In this way we obtain eventually

$$\frac{\partial q}{\partial t} = \overline{A}_z(D\omega'/l)(Q + iR)\exp\left[-i(\omega t - \phi_z)\right], \quad (5)$$

where $$Q = \frac{\sinh 2\omega' l - \sin 2\omega' l}{\cos 2\omega' l + \cosh 2\omega' l}$$

and $$R = \frac{\sinh 2\omega' l + \sin 2\omega' l}{\cos 2\omega' l + \cosh 2\omega' l}.$$

The quantities $\frac{\partial X_z}{\partial z}$, $\frac{\partial^2 X_z}{\partial z^2}$ and $\frac{\partial X_z}{\partial t}$ may be found by differentiating (2).

Substituting these into (1), and combining with (5), the equation

$$\frac{d^2\overline{A}_z}{dz^2} - \frac{U}{D}\frac{d\overline{A}_z}{dz} - \frac{\omega'}{D}\left[\frac{\beta DQ}{l} - i\left(\frac{\omega}{\omega'} - \frac{\beta DR}{l}\right)\right]\overline{A}_z = 0 \quad (6)$$

is obtained for all t after the steady cyclic state is reached. A solution to (6), expressing $\overline{A}_z$ as a function of z, and involving two arbitrary constants, may quickly be obtained. Remembering that

$$X_z = \overline{A}_z\exp(-i\omega t) = A_z\exp(i\phi_z)\exp(-i\omega t),$$

and that the boundary conditions

$$X_z = A_0\exp(-i\omega t) \qquad \text{at } z = 0$$

and

$$X_z \to 0 \qquad \text{as } z \to \infty$$

must be satisfied, we get

$$X_z = A_0\exp\left[U/2\overline{D} - \sqrt{\left(\frac{S+F}{2}\right)}\right]z \cos\left\{\omega t - \left[\sqrt{\left(\frac{S-F}{2}\right)}\right]z\right\}, \quad (7)$$

where

$$F = \frac{U^2}{4D^2} + \frac{\beta\omega}{D}\left(\frac{Q}{\sigma}\right), \quad (8)$$

$$G = \frac{\omega}{D} - \frac{\beta\omega}{D}\left(\frac{R}{\sigma}\right), \quad (9)$$

$$\sigma = 2\omega' l, \quad (10)$$

$$S = \sqrt{(F^2 + G^2)}. \quad (11)$$

(One of the arbitrary constants is proved equal to zero by making use of the fact that $U/2\overline{D} < \sqrt{[(S+F)/2]}$.)

The variations of Q/σ and R/σ with σ are shown in Fig. 3. By expanding each in the form of a series it can be seen that, to within 4 per cent if $\sigma \leqslant 1$ and to within 1 per cent if $\sigma \leqslant 0{\cdot}7$, $Q/\sigma \doteqdot \sigma^2/6$ and $R/\sigma \doteqdot 1$. On the other hand, if $\sigma > 3$, $Q/\sigma \doteqdot R/\sigma \doteqdot 1/\sigma$.

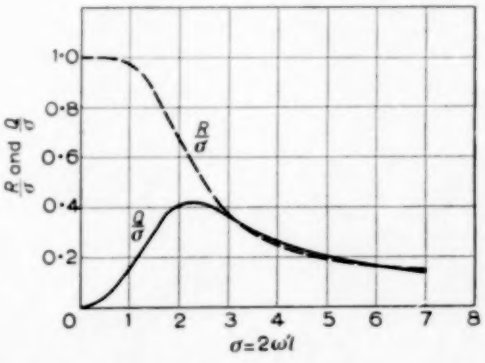

Fig. 3. The variation of R/σ and Q/σ with σ.

To proceed to the general case; if we assume that, associated with unit length of each channel, there is not volume α of pocket of depth, l, but a volume α_r of pockets each of length l_r as shown in Fig. 4.,

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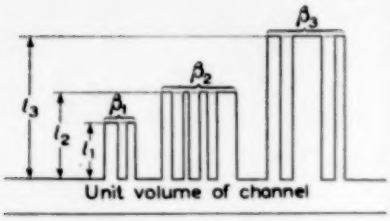

FIG. 4. A channel with relative volume β_r of pockets of length l_r.

then, by a slight extension of the above reasoning, we have

$$\left.\begin{aligned} X_z &= A_0 \exp\left[U/2\bar{D} - \sqrt{\left(\frac{S^* + F^*}{2}\right)}\right] z \\ &\quad \exp\left\{-i\left[\omega t - \sqrt{\left(\frac{S^* - F^*}{2}\right)} z\right]\right\} \\ &= A_z \exp\left[-i(\omega t - \phi_z)\right], \end{aligned}\right\} \quad (12)$$

where

$$F^* = \frac{U^2}{4\bar{D}^2} + \frac{\omega}{\bar{D}} \sum \frac{\beta_r}{2\omega' l_r} Q_r, \quad (13)$$

$$G^* = \frac{\omega}{\bar{D}} \left(1 - \sum \frac{\beta_r}{2\omega' l_r} R_r\right), \quad (14)$$

$$S^* = \sqrt{[(F^*)^2 + (G^*)^2]}, \quad (15)$$

$$\beta_r = \frac{\alpha_r}{a}, \quad (16)$$

and the problem is to determine the value of β_r for given values of l_r.

The method of analysis. It is assumed that there are a known number of identical channels in the system of length L, each with its associated pockets. Then from (12), putting $z = L$,

$$\ln\left(\frac{A_L}{A_0}\right) = \left[\frac{U}{2\bar{D}} - \sqrt{\left(\frac{S^* + F^*}{2}\right)}\right] L, \quad (17)$$

$$\phi_L = \sqrt{\left(\frac{S^* - F^*}{2}\right)} L. \quad (18)$$

Both quantities on the L.H.S. are measurable, so that the values of F^*, S^*, and hence of G^*, can be calculated, (assuming that U and $\bar{D}$ are known).

Hence from equations (13) and (14) the values of $\Sigma \beta_r (Q_r/2\omega' l_r)$ and $\Sigma \beta_r (R_r/2\omega' l_r)$ may be calculated. Denoting $Q_{jr}/2\omega' l_r$ by η_{jr} and $\Sigma \beta_r (Q_{jr}/2\omega_j' l_r)$ by μ_j, (where j signifies that a quantity depends upon the value of the angular velocity ω_j), the steps in the calculation are to choose n values of l_r.

From the measured values of the attenuation and phase-angle shift, at any value of ω_j, the value of μ_j, and the values of η_{jr} for all values of r, are calculated.

This procedure is repeated for other values of the frequency, $\omega_1 \ldots \omega_j \ldots \omega_n$. From these a set of n linear equations may be written down;

$$\mu_1 = \beta_1 \eta_{11} \ldots\ldots \beta_r \eta_{1r} \ldots\ldots \beta_n \eta_{1n} \quad (19.1)$$

$$\mu_j = \beta_1 \eta_{j1} \ldots\ldots \beta_r \eta_{jr} \ldots\ldots \beta_n \eta_{jn} \quad (19.j)$$

$$\mu_n = \beta_1 \eta_{n1} \ldots\ldots \beta_r \eta_{nr} \ldots\ldots \beta_n \eta_{nn} \quad (19.n)$$

and the values of β_r corresponding to l_r, for r having the values 1 to n, may be found by setting up the determinants of the coefficients in these simultaneous equations in the usual way.

Further, the fractional volume of "dead-space" to total empty space is $\Sigma \beta_r/(1 + \Sigma \beta_r)$.

Model 2. Channels of different lengths and diameters

The model consists of a number of channels of different lengths and radii. There are no pockets of stagnant liquid.

Let there be n_{qr} channels of length l_r and radius R_q, and let the volume flow rate in the (q, r) channel be V_{qr}. If the concentration of solute at the inlet to all channels is varying sinusoidally, then, at the end of the (q, r) channel, the concentration at any time (varying about the time-average value), will be

$$X_{qr} = A_{qr} \cos(\omega t - \phi_{qr}).$$

If the liquid issuing from all the channels at any time t is rapidly mixed, the concentration of the mixture will be given by

$$X_L = A_L \cos(\omega t - \phi_L) = \frac{\sum_r^{} \sum_q^{} n_{qr} V_{qr} A_{qr} \cos(\omega t - \phi_{qr})}{V}, \quad (20)$$

where L denotes the measured value at the exit of a bed of length L, and

$$V = \sum^{r} \sum^{q} n_{qr} V_{qr} = \text{total flow rate.}$$

By expanding (20) trigonometrically we have

$$A_L \cos \phi_L = \frac{\sum^{r} \sum^{q} n_{qr} V_{qr} A_{qr} \cos \phi_{qr}}{V} \tag{21}$$

and $$A_L \sin \phi_L = \frac{\sum^{r} \sum^{q} n_{qr} V_{qr} A_{qr} \sin \phi_{qr}}{V}. \tag{22}$$

The magnitudes of A_{qr} and ϕ_{qr} for given conditions will depend upon whether diffusion in the channel plays an important part or not. If diffusion plays only a small part then, for laminar flow in a circular tube, it can be shown that

$$A_{qr} \cos \phi_{qr} = A_0 \left[\cos \lambda_{qr} - \lambda_{qr} \sin \lambda_{qr} + \lambda_{qr}^2 \operatorname{Ci}(\lambda_{qr})\right] \tag{23}$$

$$A_{qr} \sin \phi_{qr} = A_0 \left\{\sin \lambda_{qr} + \lambda_{qr} \cos \lambda_{qr} - \lambda_{qr}^2 \left[\pi/2 - \operatorname{Si}(\lambda_{qr})\right]\right\}, \tag{24}$$

where $\lambda_{qr} = \omega l_r / [(U_0)_{qr}]$, U_0 = maximum velocity (along axis of channel),

$\operatorname{Ci}(x)$ is the cosine integral of x,

$\operatorname{Si}(x)$ is the sine integral of x,

for which values are given in tables of functions. These two equations, combined to eliminate ϕ, give the solution to equation (24) of Kramers and Alberda [6] who give a curve (their Fig. 3), showing the variation of A/A_0 with $2\omega l/U_0$; (present author's symbols).

On the other hand, if longitudinal diffusion is of importance, then A_{qr} and ϕ_{qr} may be obtained by putting $\beta_r = l_r = 0$ into equation (12) (remembering that, when $l = 0$, $Q/2\omega' l = 0$ and $R/2\omega' l = 1$), to get

$$A_{qr} \begin{matrix}\sin \\ \cos\end{matrix} \phi_{qr} = A_0 \exp\left[\sqrt{F'} - \sqrt{(S'/\lambda + F'/2)}\right] l_r \begin{matrix}\sin \\ \cos\end{matrix} \left[\sqrt{(S'/\lambda - F'/2)}\right] l_r \tag{25}$$

where

$$F' = \frac{U_{qr}^2}{4(D_{qr})^2}, \tag{26}$$

$$G' = \frac{\omega}{D_{qr}}, \tag{27}$$

$$S' = \sqrt{[(F')^2 + (G')^2]}. \tag{28}$$

(cf. The definitions of F^*, G^* and S^* given by equations (13), (14) and (15).)

The longitudinal diffusivity is written as D_{qr} because it depends not only on the molecular diffusivity but also upon the diameter and length of the pore and upon the velocity of the fluid. The magnitude of the effective longitudinal diffusivity has been discussed by Taylor [8, 9], Bosworth [10] and Van Deemter *et al.* [11] for laminar flow, and by Taylor [12] and Keyes [7] for turbulent flow. Levenspiel and Smith [13] give a general treatment and McHenry and Wilhelm [5] deal with a packed bed rather than a single tube.

For the sake of developing the argument we need an analytical expression for D_{qr}. Using the one proposed by Taylor [9] (and remembering that certain conditions must obtain for it to be valid), then

$$D_{qr} = \frac{R_q^2 (U_0)_{qr}^2}{192 D} \tag{29}$$

for laminar flow in a circular tube. If we make the reasonable assumptions that the pressure drop between the ends of every pore is the same and is given by Poiseuille's equation then

$$V_{qr} = \frac{\pi R_q^4 p}{l_r \bar{\mu} \xi}, \tag{30}$$

where p is the pressure-drop, ξ is a constant which depends upon the cross-sectional shape of the pores, and $\bar{\mu}$ is the viscosity. Further

$$n_{qr} \frac{R_q^4}{l_r} = \frac{H \epsilon_{qr}}{\pi} \left(\frac{R_q}{l_r}\right)^2, \tag{31}$$

where ϵ_{qr} is the fractional voidage contributed by n_{qr} channels of length l_r and radius R_q, and H is the total volume of the packed bed. Also

$$\lambda_{qr} = \bar{\mu} \omega l_r^2 \xi / (2 R_q^2 p). \tag{32}$$

For the convenience of the algebra let

$$N_j = \left(\frac{48 D \xi^2 \bar{\mu}^2}{p^2}\right) \omega_j \tag{33}$$

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$$M = \frac{24\,\xi\,D\,\bar{\mu}}{p} \qquad (34)$$

and it will be seen that numerical values can be put on M and N. Using equations (21) to (34) the amplitude and phase angle at the outlet end of the system can be given by expressions which involve (a) quantities which are known and (b) the minimum number of unknown variables. We get, for the case where longitudinal diffusion is small,

$$V\xi A_L \cos\phi_L/(pHA_0) = \sum^{r}\sum^{q}[\epsilon_{qr}\,R_q^{\,2}/l_r^{\,2}]$$
$$[\cos\lambda_{qr} - \lambda_{qr}\sin\lambda_{qr} + \lambda_{qr}^{\,2}\,\mathrm{Ci}\,(\lambda_{qr})] \qquad (35)$$

(similarly for $A_L \sin\phi_L$) and, for the case where diffusion is appreciable,

$$\frac{V\xi}{pH}\frac{A_L}{A_0}\cos\phi_L = \sum^{r}\sum^{q}\epsilon_{qr}\left(\frac{R_q}{l_r}\right)^2 \exp\cdot\left(\frac{Ml_r^{\,2}}{R_q^{\,4}}\right.$$
$$\left.\{1-\sqrt{(1+\sqrt{[1+(N_j^{\,2}/M^4)\,R_q^{\,4}]})}\}\right)$$
$$\cos\left\{\frac{Ml_r^{\,2}}{R_q^{\,4}}\sqrt{\left(\frac{\sqrt{[1+(N_j^{\,2}/M^4)\,R_q^{\,4}]}-1}{2}\right)}\right\}, \qquad (36)$$

and these equations can be used to analyse the distribution of pore lengths and diameters in a way similar to that described for the first model for the analysis of the distribution of pocket sizes.

For if μ_j = L.H.S. of equation (35) or (36), and η_{qrj} = the R.H.S. of equation (35) or (36), with ϵ_{qr} omitted, then, at any value of ω_j,

$$\mu_j = \sum^{r}\sum^{q}\epsilon_{qr}\eta_{qrj}$$

So certain values of R_q are chosen (the order of magnitude being known), and for each value of R_q certain values of l_r are chosen, and for each combination of R and l one calculates the value of η_{qrj} for a particular value of ω_j. μ_j contains only known or measurable quantities, so the simultaneous equations

$$\mu_j = \epsilon_{11}\,\eta_{111} + \ldots\ldots + \epsilon_{1n}\,\eta_{1n1} \text{ etc.}$$

can be written down and solved for ϵ_{qr}.

As a check, the condition

$$\epsilon = \sum^{r}\sum^{q}\epsilon_{qr}$$

must be satisfied; (ϵ can easily be measured). There is also a check on the value of ξ chosen for

$$V = Hp/\xi\bar{\mu}\,\sum^{r}\sum^{q}(R_q/l_r)^2\,\epsilon_{qr},$$

and V can be measured.

Note that equation (35) will not differentiate between pores having the same ratio of length to diameter (since l/R is involved), but equation (36) will do so.

In view of the disadvantage coupled with the use of equation (35) as given and because of the amount of computation involved by using a range of values of R_q, it is convenient to use a single mean value of R, which seems a justifiable step in most cases.

Then (35) becomes

$$\frac{V\xi}{Hp}\frac{A_L}{A_0}\cos\phi_L =$$
$$\sum^{r}\epsilon_r\left(\frac{R}{l_r}\right)^2[\cos\lambda_r - \lambda_r\sin\lambda_r + \lambda_r^{\,2}\,\mathrm{Ci}\,(\lambda_r)] \qquad (37)$$

for the case where diffusion is small, where $\lambda_r = \bar{\mu}\xi\omega\,l_r^{\,2}/(2pR^2)$ and (36) becomes

$$\frac{V\xi}{Hp}\frac{A_L}{A_0}\cos\phi_L = \sum^{r}\epsilon_r\left(\frac{R}{l_r}\right)^2$$
$$\exp\left\{\frac{Ml_r^{\,2}}{R^4}\left[1-\sqrt{\left(\frac{1+\sqrt{[1+(N_j^{\,2}/M^4)R^4]}}{2}\right)}\right]\right\}$$
$$\cos\left[\frac{Ml_r^{\,2}}{R^4}\sqrt{\left\{\frac{1}{2}\left(\sqrt{\left[1+\frac{N_j^{\,2}}{M^4}\,R^4\right]}-1\right)\right\}}\right] \qquad (38)$$

for the case where diffusion is appreciable. Then we have

$$\mu_j = \sum^{r}\epsilon_r\,\eta_{rj}$$

which, on writing out in the form of simultaneous equations for various values of ω_j, needs fewer terms in the sequence.

The checks will be as before.

SOME FURTHER CONSIDERATIONS

In the treatment of model 1 it was necessary to put a value on U. This may be done either by (a) arranging the flow in the channels to be laminar and such that diffusion plays only a small part. A value of R/L_e for the (identical) channels may be determined by using equation

(37). If a value is put on L_e (by assuming a "tortuosity factor") and hence on R, then, since

$$V = Cp\,\pi\,R^4/(L_e\,\mu\xi),$$

where V = volume flow rate,
ξ = constant; usually between 2·5 and 3·0 [1],
C = number of channels,
L_e = effective length of the channel,

a value can be put on C and hence on U.

Since the velocity at the walls is zero, the concentration does not change at the walls or beyond; i.e. the pockets do not contribute. This method assumes that the fractional volume of dead space is unaltered when the flow in the channels alters.

(b) making σ large; for, from equations (7), (8) and (9) it will be seen that if σ is made large, Q/σ and R/σ become small and the pockets again will not contribute. The system then approximates to that of model 2. In this method the velocity in the channels is unchanged.

Conclusion

A method has been suggested whereby a flow structure or a physical structure may be analysed in terms of models which have to be chosen so that they approximate to the system under investigation and whose effect on a flow of fluid containing a sinusoidally varying concentration of solute may be mathematically analysed. The attenuation and phase angle of the output streams (assumed rapidly mixed in a small mixer) are measured at a number of different frequencies and for each frequency an equation, derived from a consideration of the effect of the model on the sine-wave, is set up in the form given, for example, by equations (19.1) to 19.n); one of the coefficients (η_{jr}) contains r-dependent terms, the values of which are known (or assumed and afterwards checked) and j-dependent terms. The unknowns (β_r) are what it is wanted to find. The constant for the equation (μ_j) contains only terms which are known or measurable at the particular frequency, ω_j.

The number of values of the frequency is equal to the number of values that are given to the r-dependent part of η_{jr} so that the simultaneous equations are soluble.

The decision as to the number of values to give to r depends upon the closeness of the approximation desired, the upper limit being determined by the amount of computation or by experimental limitations.

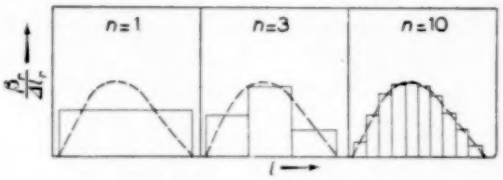

Fig. 5. Typical histograms of the distribution of relative volumes β_r of pocket length l_r.

As an illustrative example, Fig. 5 shows what might be the actual distribution curve (volume against depth) for pockets associated with a channel, and the histograms obtained by making one, three and ten determinations at these numbers of frequencies, and solving one, three and ten simultaneous equations respectively.

Results have been given for models which illustrate the method and which are likely to be useful in practice, but the choice of model and the interpretation of the results will depend upon the problem in hand. For example, it might be suspected that a catalytic reactor has an appreciable fraction of its void space "dead" i.e. filled with stagnant fluid. An analysis based on model 1 would give the fraction of dead-space as if the reactor were actually of this model form. In practice this will not be true; e.g. the dead-spaces will not be of prismatic cross-section, but the analysis will give some useful quantitative results, which would be even more useful if they were applied to the comparison of two roughly similar reactors.

On the other hand the reactor may be suspected not of having dead spaces but of having channels in which some of the fluid spent too long, and others in which it spent too short, a time. An investigation, based on model 2 would give a distribution of channel lengths and diameters as if the reactor were of this form.

As pointed out above, the model can be

changed, even for the same reactor (for example), by altering the conditions; viz. frequency or velocity of fluid, but care must be taken that the system does not change also.

The choice of magnitudes (in particular of velocity), will depend upon the physical quantities, which would in general be known roughly (e.g. channel diameter), and upon the conditions desired. For example it might be desired to use an analysis in which diffusion in the channels was important, and a velocity would have to be chosen to make this so.

In general it would be true that the nearer the chosen model approached actuality, the more difficult the mathematical analysis and the more laborious the calculations.

Acknowledgements—The statement of the problem and suggestions for the theoretical and practical methods of attack are due to Dr. J. A. STORROW.

The author is indebted to his colleague, Mr. O. E. POTTER, for very helpful suggestions and criticisms.

NOTATION

a = Cross-sectional area of a channel
A = Amplitude
$\overline{A}$ = Complex amplitude = $Ae^{i\phi}$
C = Number of identical channels
$\mathrm{Ci}(x)$ = Cosine integral
$\overline{D}$ = Generalized longitudinal diffusivity
D = Molecular diffusivity
$F = \left(\frac{U}{2\overline{D}}\right)^2 + \frac{\beta\omega Q}{2\overline{D}\omega' l}$
$F^* = \left(\frac{U}{2\overline{D}}\right)^2 + \frac{\omega}{\overline{D}} \sum_1^n \frac{\beta_r Q_r}{2\omega' l_r}$
$F' = (U/2\overline{D})^2$
$G = \frac{\omega}{\overline{D}}(1 - \beta R/[2\omega' l])$
$G^* = \frac{\omega}{\overline{D}}\left(1 - \sum_1^n \beta_r R_r/(2l_r\,\omega')\right)$
$G' = \frac{\omega}{\overline{D}}$
H = Total volume of bed
l = Length of a pocket (model 1)
l = Length of a pore (model 2)
L = Length of channel (model 1)
L_e = Effective length of a channel
m = Hydraulic radius
$M = 24\,\xi\,D\,\overline{\mu}/p$
$N_j = 48 D\xi^2\,\omega_j\,\overline{\mu}^2/p^2$
$P = \left(\frac{\cosh 2\omega' y + \cos 2\omega' y}{\cosh 2\omega' l + \cos 2\omega' l}\right)^{\frac{1}{2}}$
p = Pressure drop
q = Average concentration in a pocket
$Q = \frac{\sinh 2\omega' l - \sin 2\omega' l}{\cosh 2\omega' l + \cos 2\omega' l}$
$R = \frac{\sinh 2\omega' l + \sin 2\omega' l}{\cosh 2\omega' l + \cos 2\omega' l}$ (model 1)
R = Radius of a channel (model 2)
$S = \sqrt{[F^2 + G^2]}$
$S^* = \sqrt{[(F^*)^2 + (G^*)^2]}$
$S' = \sqrt{[(F')^2 + (G')^2]}$
$\mathrm{Si}(x)$ = Sine integral
t = Time
U = Average velocity
U_0 = Maximum velocity
V = Volume rate of flow
X = Concentration relative to a mean value
y = Distance from closed end of a pocket
z = Distance along channel
α = Volume of pockets in unit length of channel
$\beta = \alpha/a$
ϵ = Voidage
$\eta = Q/2\ \omega' l$ (model 1)
η = Defined by equations (35) or (36) et seq. (model 2)
θ = Phase angle
$\lambda = \omega l/2U_0$
$\mu = \Sigma\,\beta_r Q_r/(2\omega' l_r)$ (model 1)
$\mu = V\xi A_L/(pHA_0)\cos\phi_L$ (model 2)
$\overline{\mu}$ = Dynamic viscosity
ξ = Constant
$\sigma = 2\omega' l$
ϕ = Phase angle
ω = Angular velocity
$\omega' = \sqrt{(\omega/[2D])}$. Dimensions : L^{-1}

Subscripts

j = Identifies a value of ω
L = Value at exit of bed
o = Value at entrance to bed
q = Identifies a radius of a channel (model 2)
r = Identifies length of a pocket (model 1)
r = Identifies a length of a channel (model 2)
y = Value at distance y from closed end of pocket
z = Value at distance z along channel

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Correlation of scraped-film heat transfer in the votator

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Abstract—This work on a votator was undertaken to correlate the scraped film coefficient of heat transfer, h_s, with operating conditions, plant dimensions and physical properties of the fluid. All the available data, which include runs on the cooling of glycerol, water and two similar glyceride oils in four votator-assemblies, are provisionally correlated by the dimensionless equation :

$$\frac{h_s D_t}{k} = 4{\cdot}9 \left(\frac{D_t v\ \rho}{\mu}\right)^{0{\cdot}57} \left(\frac{c_p\ \mu}{k}\right)^{0{\cdot}47} \left(\frac{D_t N}{v}\right)^{0{\cdot}17} \left(\frac{D_t}{L}\right)^{0{\cdot}37}$$

The ratio of shaft to tube diameter, D_s/D_t, varied little throughout the work, from 0·75 to 0·81, so that any effect of this ratio is included in the constant of 4·9.

There is some indication however, of the existence of flow regimes analogous to streamline, transitional and turbulent conditions in flow through conduits and in conventional liquid mixing operations. This evidence indicates that exponents on the groups $D_t N/v$ and $D_t v\ \rho/\mu$ are higher in the turbulent range than the values appearing in the above equation.

Résumé—Ce travail sur un " votator," a été entrepris dans le but de relier le coefficient d'échange de chaleur à travers le film balayé, h_s, aux conditions opératoires, propriétés physiques du fluide et caractéristiques de l'appareil. Toutes les donnés, disponibles, comprenant des essais le refroidissement du glycerol, de l'eau et de deux glycerides homologues dans quarte assemblages de votators, satisfont à la relation sans dimension suivante :

$$\frac{h_s D_t}{k} = 4{,}9 \left(\frac{D_t v\ \rho}{\mu}\right)^{0{,}57} \left(\frac{c_p\ \mu}{k}\right)^{0{,}47} \left(\frac{D_t N}{v}\right)^{0{\cdot}17} \left(\frac{D_t}{L}\right)^{0{,}37}$$

Le rapport de l'arbre au diamètre du tube D_s/D_t a peu varié au cours de ces travaux (de 0,75 à 0,81), de telle sorte que la constante 4,9 suffit à rendre compte du phénomène pour cette faible variation.

Il existe cependant quelques indications sur les régimes d'écoulement analogues aux régimes laminaires transitoires et turbulents dans les conduites et dans les opérations de mélange.

Ces remarques montrent que les exposants des groupes $D_t N/v$ et $D_t v\ \rho/\mu$ sont plus grands en régime turbulent que les valeurs mentionnées dans l'équation précitée.

Zusammenfassung—Diese Untersuchung an einem Votator wurde unternommen, um die Wärmeübergangszahl beim Abstreifen, h_s, mit den Arbeitsbedingungen, den Abmessungen der Anlage unde den physikalishchen Eigenschaften der Flüssigkeit in Beziehung zu setzen. Alle verfügbaren Daten, in denen Versuche über die Kühlung mit Glyzerin, Wasser und zwei ähnlichen Glyzerin-Ölen in vier Votatoranordnungen enthalten sind, können vorläufig durch folgende dimensionslose Beziehung dargestellt werden.

$$\frac{h_s D_t}{k} = 4{,}9 \left(\frac{D_t v\ \rho}{\mu}\right)^{0{,}57} \left(\frac{c_p\ \mu}{k}\right)^{0{,}47} \left(\frac{D_t N}{v}\right)^{0{,}17} \left(\frac{D_t}{L}\right)^{0{,}37}$$

Das Verhältnis von Schaft – zu Rohrdurchmesser (D_s/D_t) ändert sich nur wenig innerhalb dieser Untersuchungen, nämlich von 0,75 bis 0,81, so dass ein etwaiger Einfluss dieses Quotienten in der Konstaten 4,9 enthalten ist.

Es gibt einige Anzeichen für die Existenz von Strömungsbereichen ähnlich der laminaren, Übergangs – und turbulenten Form bei der Kanalströmung oder den üblichen Mischverfahren von Flüssingkeiten. Im turbulenten Bereich sind nämlich die Exponenten der Kenngrössen $D_t N/v$ und $D_t v\ \rho/\mu$ höher als sie in der obigen Gleichung erscheinen.

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Introduction

The Votator, a double-pipe, scraped surface heat exchanger, is widely used in the food and chemical industries, for example in the crystallizing of petroleum waxes, the plasticizing of margarine and shortenings and in sulphation and sulphonation reactions.

Despite its widespread applications, only one paper has been found dealing quantitatively with heat transfer in the votator. This paper, by Houlton [6], deals with a water-to-water heat exchange in a small laboratory unit, in which shaft speed, jacket water velocity and throughput rates were studied in relation to the over-all and film heat transfer coefficients.

No correlation of the scraped film coefficient of heat transfer with operating conditions and physical properties has previously appeared, although the need for such a correlation was underlined thirteen years ago by Houlton, whose data is used in the present work.

Many of the present data were obtained incidentally during work on a more extensive investigation. If the study of heat transfer through the scraped film had been the prime object of that work, cooling would have been effected by brine rather than by direct-contact ammonia evaporation, thus simplifying measurement of the heat transferred. In an ideal case also the fluids on the scraped surface side would have been chosen to avoid phase change.

Experimental Work

Apparatus

Two ammonia-cooled votators were used, they were structually similar and the small unit is shown in Fig. 1. They were designed by the Girdler Corporation (U.S.A.) and made by A. Johnson & Co. (London) Ltd., the details being as follows

Table 1

Votator	*Small laboratory unit*	*Large unit*
No. of tubes in series	1	2 or 3
" Effective " scraped area, A_e(ft^2)	0·687	7·99 11·98
Heat transfer tube o.d. (in.)	3·25	4·375 4·375
Heat transfer tube i.d. (in.)	3·00	4·00 4·00
Revolving shaft o.d. (in.)	2·25	3·25 3·25
A. Johnson & Co. specification no.	3/41*A*	*M*123*A*

Attached to each shaft and 180° apart were two scraper blades of the " floating " type, which moved freely to the wall under centrifugal force and fluid kinetic pressure as the shaft revolved. (The shaft plus blades is called the mutator).

The votator tubes were made of mild steel with thinly chromium plated inner surfaces.

Materials used and their physical properties

Water and glycerol. Since the glycerol contained a small but unknown quantity of water its viscosity was measured in a Ferranti viscometer ; the results are shown in Fig. 8. For the other physical properties those for pure glycerol were used. Two similar glyceride oils, *A* and *B*, were also used and the following typical values were taken for their physical properties :

Specific heat : (partially crystalline oil beyond votator) 0·45 B.t.u./lb °F

Specific heat : (less crystalline oil within votator) 0·5 B.t.u./lb °F [3]

Latent heat of fusion : 95 B.t.u./lb.

Thermal conductivity : 0·1 B.t.u./hr ft^2 °F/ft [3]

Specific gravity : 0·89.

Progressive crystallizing of the oils along the votator, plus substantial super-cooling, prevented accurate assessment of an average viscosity within the device.

Values in Fig. 9 for similar oils at temperatures above cloud point [9] were extrapolated through about 20°F to provide values within the relevant temperature range. A reason for accepting this procedure is given later.

The equilibrium percentage solid content at a given temperature was estimated experimentally as " Solid Content Index " (S.C.I.) using the method and terminology of Fulton, Lutton and Wille [4].

Measurements were as follows :

Table 2

	Oil A	*Oil B*
S.C.I. at 60°F	14·8	17·5
S.C.I. at 92°F	8·5	9·7

Linear interpolation has been found to give a good approximation between these temperatures for these oils [9].

Determination of the experimental scraped film coefficients

Experimental conditions and results from runs on the small votator appear in Table 3, values calculated from Houlton's runs are given in Table 4, while values obtained on the large votator are given in Table 5.

Table 3. Experimental results obtained with the small votator. Votator outlet temperature : 65°F, $D_t/L = 0{\cdot}286$

Run no.	*Mutator* (rev/hr)	*Flow rate* (lb/hr)	*Votator inlet temp.* (°F)	*Maximum final temp.* (°F)	*Ammonia temp.* (°F)	*Over-all heat transfer coeff.* U (B.t.u./ft² hr °F)	*Ammonia film transfer coeff.* h_{NH_3} (B.t.u./ft² hr °F)	*Scraped film transfer coeff.* h_s (B.t.u./ft² hr °F)	$\frac{h_s D_t}{k}$	$\frac{D_t v \rho}{\mu}$	$\frac{c_p \mu}{k}$	$\frac{D_t N}{v}$
1	27,000	210	118	77·4	29	208	957	297	741	17·9	705	37·5
2	27,000	248	116	77·6	26	224	1016	324	810	21·1	705	31·5
3	27,000	300	113·5	75·1	12	220	1115	308	770	25·6	705	26·0
4	27,000	352	115	74·6	12	256	1277	367	916	30·05	705	22·1
5	16,500	180	114	80·3	34	179	785	256	640	15·35	705	26.42
6	16,500	210	114	78·8	29	189	858	268	670	17·9	705	22·7
7	16,500	255	118	78·0	22	206	1000	290	725	21·75	705	18·67
8	16,500	300	115	78.4	21	227	1062	327	817	25·6	705	15·87
9	16,500	360	115	80·4	14	229	1135	325	813	30·7	705	13·21
10	16,500	443	116	83·0	9	248	1235	355	887	37·75	705	10·75
11	12,900	180	114	77·0	31	180	820	254	635	15·35	705	20·67
12	12,900	210	115	78·0	26	184	885	249	622	17·9	705	17·7
13	12,900	255	115·5	77·4	23	210	995	298	744	21·75	705	14·6
14	12,900	300	118	81·3	16	206	1073	284	710	25·6	705	12·4
15	12,900	360	118	83·8	12	218	1125	303	757	30·7	705	10·35
16	12,900	427	117	87·4	6	215	1163	295	737	36·45	705	8·7
17	9000	180	116	78·3	44	237	840	380	950	15·35	705	14·42
18	9000	255	116·5	82·2	26	199	936	281	703	21·75	705	10·2
19	9000	300	118	83·1	22	216	1030	306	765	25·6	705	8·66
20	9000	360	115	88·8	9	216	1141	297	742	30·7	705	7·22
21	9000	435	117	90·6	2	198	1130	266	665	37·1	705	5·97
22	7500	180	114	77·6	29	170	798	237	592	15·35	705	12·0
23	7500	210	115	81·2	27	176	844	244	610	17·9	705	10·3
24	7500	255	118	84·1	26	197	940	277	692	21·75	705	8·47
25	7500	300	115	86·6	16	180	941	245	613	25·6	705	7·2
26	7500	360	116	88·2	22	224	1049	321	803	30·7	705	6·0
27	7500	427	124	91·7	15	252	1235	362	905	36·45	705	5·05
28	5400	172	116	81·0	31	165	784	228	570	14·7	705	9·05
29	5400	210	118·5	87·9	34	184	817	263	658	17·9	705	7·43
30	5400	255	125	86·6	27	206	970	292	730	21·75	705	6·12
31	5400	300	119	90·0	22	191	938	265	663	25·6	705	5·2
32	5400	360	119	92·8	15	202	1052	278	695	30·7	705	4·33
33	5400	435	120·5	93·6	14	240	1194	341	855	37·1	705	3·58
†34	12,900	300	121	—	16	344	1515	540	372	20·20	4·91	13·94
‡35	7200	180	116	—	22	129	719	168	256	2·72	2790	16·33
36	7200	255	118·5	—	10	155	899	203	310	3·86	2790	11·53
37	7200	360	118·5	—	−1	187	1095	248	378	5·45	2790	8·16
38	27,000	180	120	—	29	167	810	229	349	2·72	2790	61·2
39	27,000	255	120	—	22	200	988	279	425	3·86	2790	43·25
40	27,000	360	118	—	6	213	1150	292	445	5·45	2790	30·6

* Material cooled in runs 1 — 33 was Oil *A*.
† Material cooled in run 34 was water.
‡ Material cooled in runs 35 — 40 was aqueous glycerol.

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Table 4. Values calculated from data published by HOULTON [6]
The material cooled and the coolant were water. In the six runs below, $D_t/L = 0{\cdot}281$

Mutator (rev/hr)	*Average linear velocity of water being cooled* (ft/hr)	*Scraped film transfer coeff.* h_s (B.t.u./ft^2 hr °F)	$\frac{h_s D_t}{k}$	$\frac{D_t v\,\rho}{\mu}$	$\frac{c_p\,\mu}{k}$	$\frac{D_t N}{v}$
18,000	449·5	1110	734	6750	2·745	10
30,000	427	1550	1025	6140	2·865	17·56
42,000	434	1870	1238	6240	2·865	24·2
60,000	441	2160	1429	6350	2·865	34·0
114,000	444	3140	2078	5910	3·095	64·2
114,000	266	1800	1240	3275	3·485	107

Table 5. Experimental results obtained with the large votator.
Throughout these runs on oil B the mutator shaft speed was 750 rev/min.

Run no.	*Flow rate* (lb/hr)	*Votator inlet temp.* (°F)	*Votator outlet temp.* (°F)	*Maximum final temp.* (°F)	*Ammonia temp.* (°F)	*Overall heat transfer coeff.* U (B.t.u./ft^2 hr °F)	*Ammonia film transfer coeff.* h_{NH_3} (B.t.u./ft^2 hr °F)	*Scraped film transfer coeff.* h_s (B.t.u./ft^2 hr °F)	$\frac{h_s D_t}{k}$	$\frac{D_t v\,\rho}{\mu}$	$\frac{c_p\,\mu}{k}$	$\frac{D_t N}{v}$	$\frac{D_t}{L}$
41	3800	120	58	70·8	0	246	1278	373	1241	293	722	6·54	0·0437
42	3800	120	63	74·1	12	258	1267	403	1341	293	722	6·54	0·0437
43	3850	120	58	71·1	14	201	1009	296	985	297	722	6·45	0·0292
44	6800	119	58	71·6	− 6	260	1386	396	1320	525	722	3·66	0·0292
45	7000	121	63	74·3	0	262	1378	401	1338	540	722	3·55	0·0292
46	5000	121	56	69·8	− 1	222	1198	326	1085	386	722	4·97	0·0292
47	3900	119	58	72·1	0	243	1260	368	1225	301	722	6·37	0·0437
48	3950	120	58	71·0	14	204	1023	301	1002	305	722	6·3	0·0292
49	3900	118	56	69·8	10	198	1005	290	965	292	742	6·37	0·0292
50	3900	117	52	66·4	7	211	1058	313	1041	265	820	6·37	0·0292
51	3700	117	51	64·9	0	190	1023	272	905	251	820	6·71	0·0292
52	6800	117	58	71·0	− 6	256	1355	390	1300	510	742	3·66	0·0292

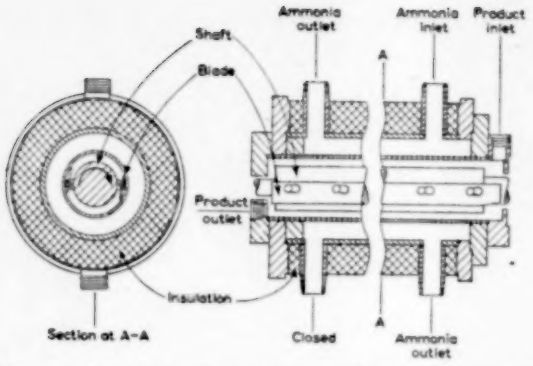

FIG. 1. Longitudinal and cross-sectional diagrams of ammonia-jacketed laboratory votator.

Over-all coefficients based on the inside scraped surface area of the votator were first calculated from the general equation :

$$Q = UA_c L.M.T.D.$$

where the "effective" scraped area, A_c, was calculated in accordance with HOULTON'S assumption [6] that the flanged heads of the refrigerant jacket were only half effective for cooling.

In the case of the glyceride oils *A* and *B*, the heat transferred per hour Q, consists of :—

Heat equivalent to about 85 per cent of the energy consumed by the mutator motor [9].

Sensible heat due to cooling the partially crystallized oil.

Latent heat resulting from some crystallization of the oil in the votator.

The fraction crystallizing in the device was calculated as the difference between the S.C.I. at the maximum temperature reached by the partially solidifying oil after emerging from the votator and the crystallization corresponding to the temperature rise beyond the votator. Allowance was made for frictional and mechanical heat effects beyond the votator from preliminary heat balance measurements.

Attempts to calculate the ammonia film coefficient either by assuming a forced convection mechanism and using the usual Dittus–Boelter equation, or by assuming a natural convection mechanism and using the usual correlation involving Nusselt, Grashof and Prandtl numbers, led to an ammonia film coefficient less than the overall coefficient—an impossible result.

It was thus concluded that a much higher ammonia film coefficient resulting from a nucleate boiling mechanism must be prevailing. This was partly confirmed by visual observations of vapour plus entrained liquid ammonia flowing upwards past a glass window in the upper outlet pipe from the ammonia jacket.

Ammonia film coefficients were therefore calculated from a correlation by MCNELLY [7], based on a nucleate boiling mechanism. The properties of the ammonia film were evaluated at the mean film temperature. If either the bulk temperature or the adjacent metal wall temperature had been used the resulting film coefficients would have differed from that corresponding to the mean film temperature by less than 2 per cent, which is well within the limits of accuracy of MCNELLY'S correlation. Scraped film coefficients were than extracted from the overall coefficients by the general equation :

$$\frac{1}{U} = \frac{1}{h_{NH_3}} + \frac{1}{h_m} + \frac{1}{h_s}$$

Here h_m is the usual metal wall coefficient, given by dividing the thermal conductivity by the metal thickness.

DIMENSIONAL ANALYSIS

Heat transfer through the scraped film will be by conduction and hence the thermal conductivity, k, of the fluid is involved. The film thickness should depend on the linear axial velocity, v, of the fluid, on fluid density, ρ, viscosity, μ, tube diameter, D_t, mutator shaft speed, N, shaft diameter, D_s, and upon the diameter of the mutator, D_m, which last is defined as twice the distance from the blade edge to the shaft axis. In view of the phase-change of some of the oil, and the possibility of modifications in flow pattern along the freezer, the tube length, l_t, and blade length l_b, may be influential factors. Also, for a given rate of heat transfer, the bulk temperature of the stream is affected by the specific heat of the fluid, c_p, which must also be included.

The dimensions chosen as fundamental in the analysis were mass, length, time, heat and temperature, necessitating the inclusion of the mechanical equivalent of heat, J – a dimensional constant. Thus the general equation relating h_s to these twelve factors in exponential form and where ϕ is a constant is :

$$h_s = \phi\,(D_m^a\, D_s^b\, D_t^c\, l_b^d\, l_t^e\, N^f\, v^g\, c_p^i\, k^j\, \rho^n\, \mu^p\, J^q) \quad (1)$$

Dimensional analysis of this relationship leads to the general equation :

$$\frac{h_s D_t}{k} = \phi \left(\frac{D_t v\, \rho}{\mu}\right)^n \left(\frac{c_p\, \mu}{k}\right)^i \left(\frac{D_t N}{v}\right)^f \left(\frac{L}{D_t}\right)^r \left(\frac{D_s}{D_t}\right)^h \quad (2)$$

l_b almost equals l_t, equals L (say), r equals d + e, q was found to be zero and the assumption has been made that D_m/D_t is unity, a point commented on later.

The Nusselt and Prandtl groups have their usual significance, while the group $D_t v\,\rho/\mu$ only resembles the Reynolds number since it contains the tube diameter, D_t, instead of the equivalent diameter of the annulus between tube and mutator shaft. The group $D_t N/v$ is the ratio of a measure of the rotary peripheral velocity to axial velocity of the fluid and the groups D_s/D_t and L/D_t partly define the geometry of the votator.

Powers of the dimensionless groups and the coefficient ϕ

Physical properties have been evaluated at average bulk fluid temperatures :

Exponent f was evaluated by using the data for oil *A* and glycerol in log – log plots of $h_s D_t/k$ vs. $D_t N/v$.

Here $D_t v\,\rho/\mu$ remained constant for each curve, $c_p\,\mu/k$ remained constant for each substance, and D_s/D_t and L/D_t remained constant throughout.

The slope of Fig. 2 shows f to be about 0·17. The significance of the line for water is discussed later.

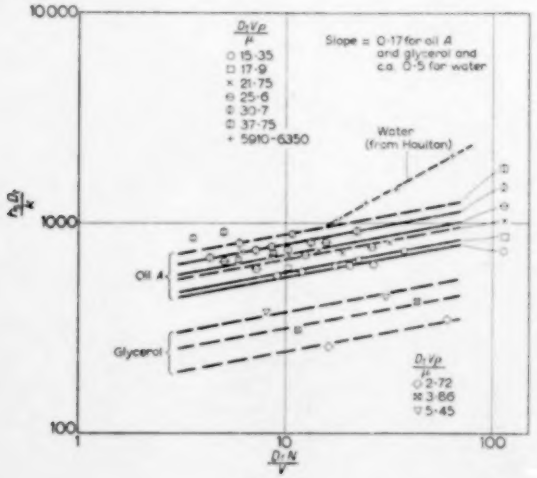

FIG. 2.

Exponent n. In a preliminary assessment of this exponent, data for glycerol and oil *A* were used in log – log plots of

$$\frac{h_s D_t}{k}\left(\frac{D_t N}{v}\right)^{-0.17} \quad \text{vs.} \quad \frac{D_t v\,\rho}{\mu}$$

where $c_p\,\mu/k$ remained constant for each curve, and D_s/D_t and L/D_t remained constant throughout.

The slope of Fig. 3 shows n to be about 0·52 ; this value was slightly revized later from a final plot of all the available data.

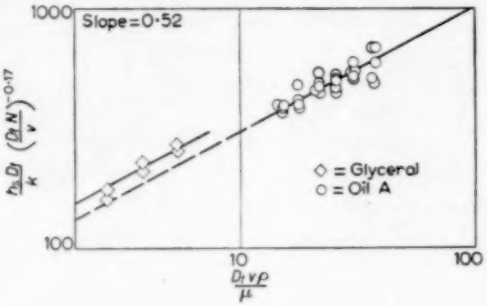

FIG. 3.

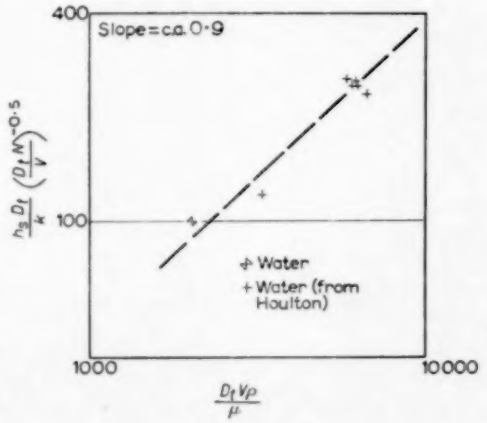

FIG. 4.

Exponent r. Data for oil *A* on the small votator were used with data for oil *B* on the large votator when either two or three tubes in series were used. This provided a range of tube lengths from 0·87 to 11·44 ft. Log – log plots were made of

$$\frac{h_s D_t}{k}\left(\frac{D_t N}{v}\right)^{-0.17}\left(\frac{D_t v\,\rho}{\mu}\right)^{-0.52} \quad \text{vs.} \quad \frac{L}{D_t}$$

assuming the same $c_p\,\mu/k$ for these two similar oils.

The ratio D_s/D_t was no longer strictly constant, but the variation is considered small, i.e. for the small votator, D_s/D_t was 0·75, while for the large unit it was 0·81.

The slope of Fig. 5 shows r to be about — 0·37.

Exponent i. For glycerol, oils *A* and *B* and water, log – log plots were made of

$$\frac{h_s D_t}{k}\left(\frac{D_t v\,\rho}{\mu}\right)^{-0\cdot52}\left(\frac{D_t N}{v}\right)^{-0\cdot17}\left(\frac{D_t}{L}\right)^{-0\cdot37} \text{ vs. } \frac{c_p\,\mu}{k}$$

A value of 0·47 was provisionally taken for i from the slope of the line in Fig. 6.

Exponent b. The effects of varying the ratio D_s/D_t were not studied and it remained nearly constant throughout both this work and that of HOULTON. The factor $(D_s/D_t)^b$ is therefore included in the value of the coefficient found below.

Coefficient ϕ and revised value for exponent n. Because of the wide range of values of $D_t v\,\rho/\mu$ covered in this work a final plot of all the data against this group was made to assess the coefficient ϕ. Fig. 7 shows a log – log plot of :

$$\frac{h_s D_t}{k}\left(\frac{D_t N}{v}\right)^{-0\cdot17}\left(\frac{c_p\,\mu}{k}\right)^{-0\cdot47}\left(\frac{D_t}{L}\right)^{-0\cdot37} \text{ vs. } \frac{D_t v\,\rho}{\mu}$$

The intercept has a value of 4·9 and the slope of the line gives a revized value for n of 0·57.

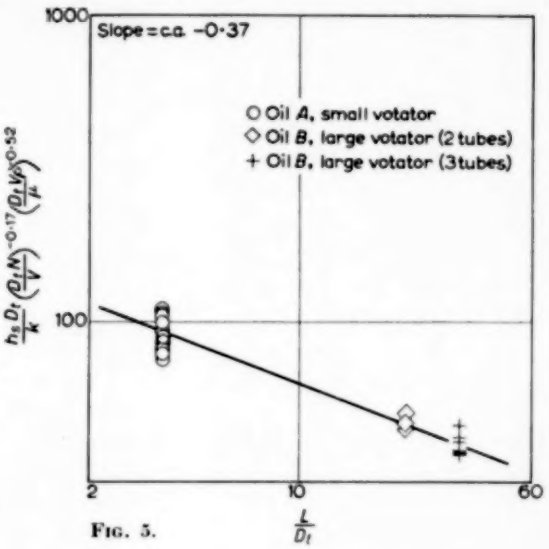

FIG. 5.

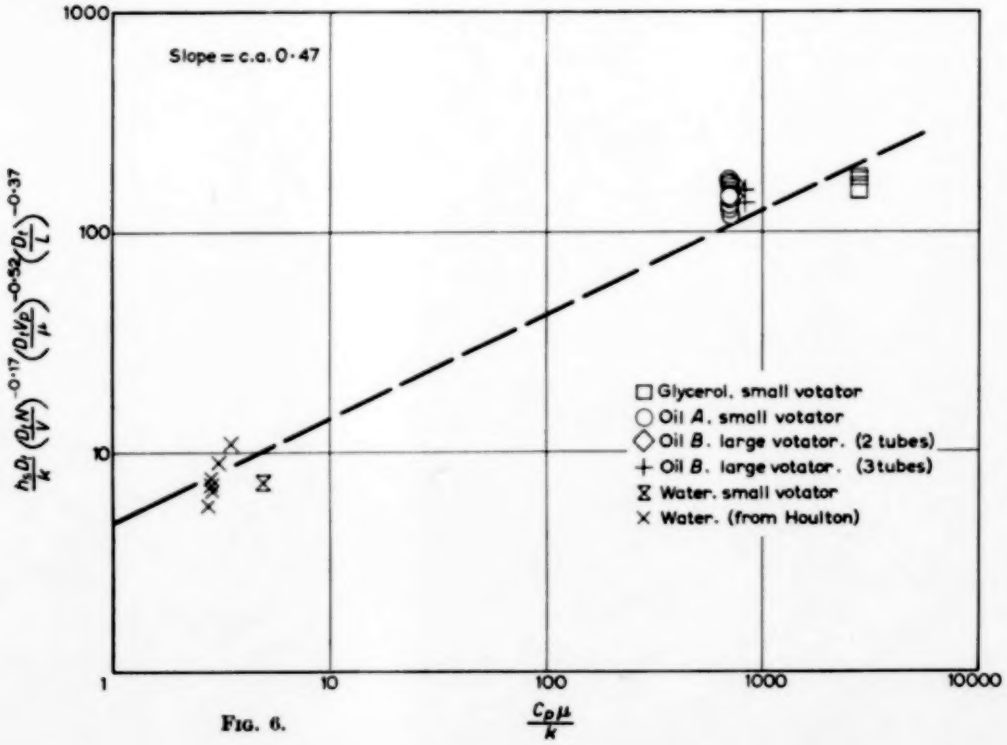

FIG. 6.

The equation relating to the line on Fig. 7, which contains all the available data, is :—

$$\frac{h_s D_t}{k} = 4{\cdot}9 \left(\frac{D_t v\,\rho}{\mu}\right)^{0{\cdot}57} \left(\frac{c_p\,\mu}{k}\right)^{0{\cdot}47} \left(\frac{D_t N}{v}\right)^{0{\cdot}17} \left(\frac{D_t}{L}\right)^{0{\cdot}37} \quad (3)$$

The equation has been determined for values of D_s/D_t between 0·75 and 0·81.

Evidence for the existence of streamline and turbulent flow regimes

It is well known that the transition between streamline and turbulent fluid flow through straight conduits is characterized by values of $D_e v\,\rho/\mu$ between 2000 and 4000, while the corresponding transition region for conventional liquid mixing vessels is defined by values of $D_i^2 N\,\rho/\mu$ between 10 and 10,000 [5].

Maximum and minimum values of these two forms of Reynolds number are shown for these runs in Table 6, where the equivalent diameter of the annulus between tube and mutator shaft, D_e, is given by $D_t - D_s$ and where the impeller diameter, D_i, is taken as D_m. From this table analogy with conventional liquid mixing vessels would indicate that turbulence is only fully developed in the case of the water runs.

Table 6. Maximum and minimum values of $(D_t - D_s)v\,\rho/\mu$ *and* $D_m^2 N\rho/\mu$

Fluid	$(D_t - D_s)\,v\,\rho/\mu$		$D_m^2 N\,\rho/\mu$	
	Min.	*Max.*	*Min.*	*Max.*
Glycerol	0·7	1·4	44·0	175·0
Oil *A*	3·7	9·4	134·0	670·0
Oil *B*	63·0	135·0	1690·0	2030·0
Water	505·0	1690·0	28200·0	380,000·0

There is also some indication of the existence of two regimes of flow in Fig. 2, where the middle four values for water from Table 4 are plotted to indicate an exponent of the order of 0·5 for the group $D_t N/v$ in the turbulent region. This exponent cannot be determined with greater precision from the available data (that of HOULTON) since, although the values of L/D_t, D_s/D_t and $c_p\,\mu/k$ corresponding to points on this line remained constant, values of $D_t\,v\,\rho/\mu$ ranged from 5910 to 6350.

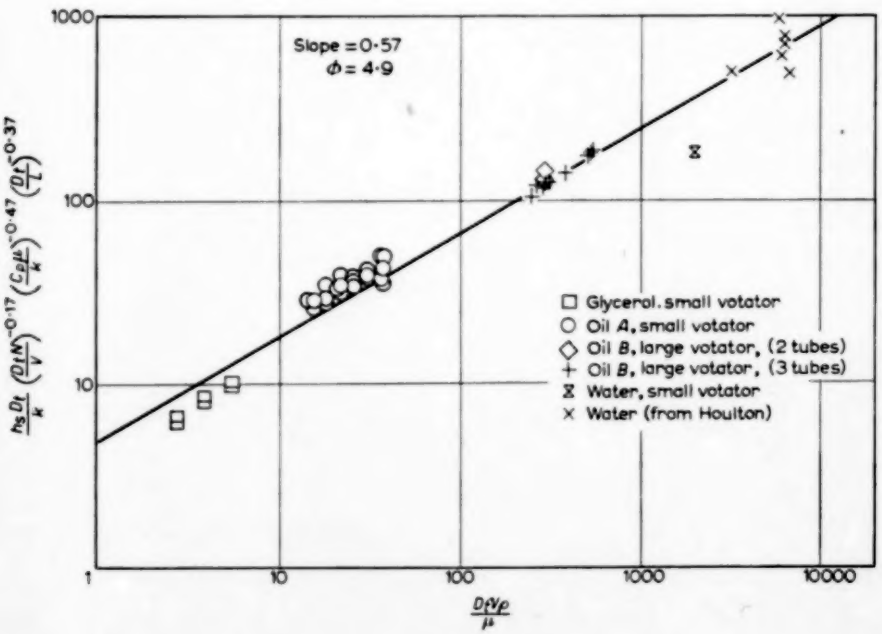

FIG. 7.

Fig. 4 suggests an exponent of the order of 0·9 for the group $D_t v\,\rho/\mu$ in the turbulent region. Although the groups L/D_t, D_s/D_t and $c_p\,\mu/k$ are constant for Fig. 4 more data are clearly needed to establish this exponent under turbulent conditions. Analogy with correlations for streamline and turbulent flow through conduits indicates that the exponent on the group L/D_t will at least be reduced for turbulent conditions, due to reduced entrance effects.

It seems from the above observations that the exponent on the Prandtl group in equation (3) may be a hybrid value obtained by combining data for streamline and turbulent flow. Accordingly the correlation must be regarded as provisional pending further data on the existence of more than one flow regime and on the various group-exponents at high Reynolds numbers.

It appears, then, that the situation regarding equation (3) may resemble that underlined by comments of PRATT [8] when comparing his own correlation with that of CHILTON, DREW and JEBENS [2] for heat transfer in agitated vessels. PRATT's comments strongly suggest that the well known single-line correlation of CHILTON, DREW and JEBENS actually spans more than one flow regime. Comments relevant to this latter topic also appear in discussions of BROWN, SCOTT and TOYNE [1].

Features of equation (3). The constants in the correlation have been found from experiments in which the fluid was being cooled. The fluid adjacent to the scraped metal wall would thus be colder and more viscous than in the main steam. Slightly different constants might be expected if the fluid were being heated, since the temperature gradient and hence the viscosity pattern would be reversed.

A comparison between the exponents on the groups $D_t N/v$ and $D_t v\,\rho/\mu$ indicates that the rate of heat transfer is not dominated by the mutator speed and that the contribution afforded by linear flow velocity through the votator must be considerable.

Logarithmic mean temperature difference

In calculating over-all coefficients from the experimental data the logarithmic mean temperature difference between ammonia and the votated fluid was used; this practice is only valid if constant specific heat can be assumed as in the case of water and glycerol. It is believed that this assumption can be largely justified in the case of oils *A* and *B* despite their partial phase change within the votator, in view of their substantially linear relationship between equilibrium solid content and temperature. Thus, over most of the temperature range through which the oil is cooled, it has an effective specific heat compounded of nearly constant amounts of latent and sensible heat.

Physical properties of oils A and B

A perfect correlation in Fig. 7 is partly prevented by the shortage of accurate physical data for oils *A* and *B*, necessitating extrapolations and the use of typical values.

In particular, since the true viscosities for oils *A* and *B* at sub-cloud-point temperatures are not known, it may be felt that the data for these substances lie on the general line of Fig. 7 by a coincidence connected with the use of " pseudo " viscosities derived from the extrapolation of Fig. 9. However, it should be noted that exponents on groups containing viscosity (namely $D_t v\,\rho/\mu$ and $c_p\,\mu/k$) have not been derived exclusively from data for oils *A* and *B*, but have been obtained independently from data for glycerol in the case of $D_t v\,\rho/\mu$ (Fig. 3) and from data for glycerol and water in the case of $c_p\,\mu/k$ (Fig. 6); true viscosities for glycerol and water are, of course, known.

Furthermore, partial cancellation in the groups $D_t v\,\rho/\mu$ and $c_p\,\mu/k$ leaves viscosity to the rather low power of $-0{\cdot}1$ which may partially account for the close agreement of data for oils *A* and *B* with the provisional correlation, despite the use of " pseudo " viscosities in place of true values for these substances.

Contact between blades and tube wall

It is known that even slight clearance between the edges of the scraper blades and the tube wall may lead to considerable reductions in heat transfer [9]. Because of the " floating " blades used in this work the assumption has been made

that close contact between blade-edges and wall is maintained; this should be true at least for water and glycerol, and by taking D_m/D_t equal to unity throughout the assumption has been extended to the partially crystallizing oils *A* and *B*.

Factors not included in the correlation

The effects of variation in mutator design have not been included, for instance with regard to the shape of the cross-section of the shaft, the variation of the ratio D_s/D_t, the number of blades, and the clearance between blade-edges and tube wall. More work is needed to incorporate the above factors and to distinguish more clearly between streamline and turbulent conditions.

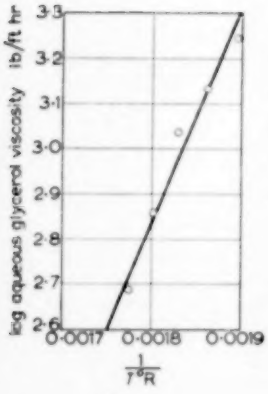

FIG. 8.

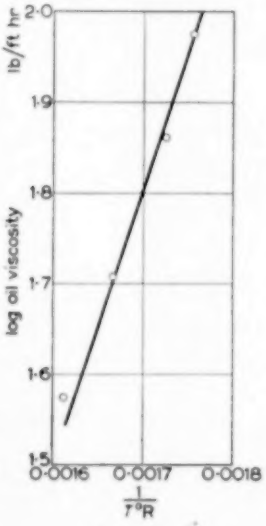

FIG. 9.

Acknowledgements—Useful comment was given by Mr. L. H. FROOMES, and the author is grateful to Mr. H. R. GALLEYMORE, Director of the Chemical Division of Thomas Hedley & Co. Ltd., for permission to publish this paper.

NOMENCLATURE

A_c	= "Effective" scraped heat transfer surface	ft²
c_p	= Specific heat	B.t.u/lb°F
D_c	= Conduit inner diameter, or equivalent diameter of an annulus	ft
D_i	= Impeller diameter	ft
D_m	= Mutator diameter (2 x distance from blade edge to shaft axis)	ft
D_s	= Diameter of mutator shaft	ft
D_t	= Internal diameter of Votator tube	ft
h_m	= Metal wall coefficient of heat transfer	B.t.u./ft²hr°F
h_{NH_3}	= Ammonia film coefficient of heat transfer	B.t.u./ft²hr°F
h_s	= Scraped film coefficient of heat transfer	B.t.u./ft²hr°F
k	= Thermal conductivity	B.t.u./ft²hr°F/ft
l_b	= Length of scraper blade (= *L*)	ft
l_t	= Length of votator tube (= *L*)	ft
L.M.T.D.	= Log. mean temperature difference between fluid being cooled and refrigerant	°F
N	= Mutator shaft speed	rev/hr
Q	= Total heat transferred/unit time	B.t.u./hr
U	= Over-all coefficient of heat transfer	B.t.u./ft²hr°F
v	= Average axial flow velocity of fluid through votator	ft/hr
ρ	= Fluid density	lb/ft³
μ	= Absolute fluid viscosity	lb/ft hr
ϕ	= A proportionality constant	–

Exponents :—
$a, b, c, d, e, f, g, i, j, n, p, q.$
$r = d + e.$

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REPORT OF MEETING

Symposium on Chemical Reaction Engineering

Syllabus—Chemical reaction engineering is a part of chemical engineering in general. It is a new branch of science which is still in the development stage. It aims at controlling the chemical conversions on a technical scale and will ultimately lead to appropriate and successful reactor design. An important part is played by various factors such as flow phenomena, mass and heat transfer, and reaction kinetics. It will be clear that in the first place it is necessary to know these factors separately. Yet this knowledge in itself is insufficient. The development of chemical conversions on a technical scale can only be understood from the relation and interaction between the above-mentioned factors. This relation and interaction will be the main theme of the symposium, "Chemical Reaction Engineering".

On 7, 8 and 9 May 1957 First European Symposium on Chemical Reaction Engineering took place in Amsterdam in the Royal Tropical Institute. This symposium, which at the same time was the twelfth conference of the European Federation for Chemical Engineering, was organized by the Chemical Engineers Section of the Koninklijk Instituut van Ingenieurs and the Chemical Technology and Industrial Chemistry Section of the Koninklijke Nederlandse Chemische Vereniging.

The members of the Symposium Committee were: Dr. Ir. J. C. Vlugter (Chairman), Prof. Ir. E. F. Boon, Dr. C. van Heerden, Dr. Ir. A. Klinkenberg, Dr. K. Rietema (Secretary), and Dr. Ir. G. S. van der Vlies (Treasurer).

There were three official languages: French, German and English. Three weeks before the symposium the members had received preprints of the fourteen contributions. These papers were dealt with in five successive sessions. Each session had a chairman as well as a rapporteur, whose task consisted in reporting on the discussions and the session.

In all, 260 members had registered for the symposium, half this number being Dutch, the other half from twelve different countries. The fact that there were three languages has not caused any difficulties, which is also due to the good offices of the linguistic adviser, Mr. W. G. de Boer.

The symposium was opened by Dr. Vlugter, who welcomed the official guests and drew attention to the pioneering work done on behalf of the European Federation for Chemical Engineering by Mr. Jean Gérard, who recently died in Paris.

Dr. Vlugter added a special word of welcome to the students, twenty-five of whom attended the symposium. Finally he expressed his confidence that the symposium would be a success.

First Session: "Introductory Papers"

Chairman Dr. Ir. J. C. Vlugter.

Rapporteur Dr. Ir. D. van Zoonen.

Speakers Prof. Dr. D. W. van Krevelen (Central Laboratorium, Staatsmijnen in Limburg); Prof. M. Letort (Faculté des Sciences de l'Université de Nancy); Prof. Ir. H. Kramers (Laboratorium voor Fysische Technologie, Technische Hogeschool, Delft).

In this session introductions to the symposium were given. The first was a general introduction by Prof. van Krevelen, who explained the aim of the symposium and gave a detailed classification of the field of study. In addition, it was shown how the various papers to be presented at the symposium fitted in this classification.

In a historical survey Prof. van Krevelen showed that three periods can be distinguished in the development of this branch of science. The first is the "empirical-phenomenological" period up to about 1915; then comes the "molecular-statistical" and, from 1937, the "technological" period.

One of the most important aspects of the technology of chemical reactors is kinetics. This can be divided into microkinetics and macrokinetics. Microkinetics deals with chemical kinetics or molecular-scale processes. To these belong : spontaneous reactions, catalysed reactions, chain reactions, as well as side reactions and consecutive reactions. Often it is not necessary, for the design and calculation of a chemical reactor, to know the chemical kinetics of all the stages of the reaction mechanism. In general it sufficies to have a general picture of the kinetics.

In the laboratory it is usually possible to make the reactions proceed under ideal conditions and to choose dispersion, homogenization as well as heat supply and removal at will. In industry this is often impossible. The problems are then complicated by mass transport, heat transfer and transfer of impulse on a larger scale than the molecular one. This is called macrokinetics, which deals with phenomena proceeding on a scale that is comparable with reactor dimensions, the dimensions of the dispersed substance or the thickness of the boundary layers.

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The influence of macro- and micro-kinetics is reflected in the way in which the reaction rate depends on temperature and pressure, in the stability of the reactor as well as in the yield and selectivity of the reactions.

Prof. VAN KREVELEN concluded with the words : " I think I may say that in this field of study, with its numerous aspects, our symposium is the most comprehensive survey ever given".

In the second introductory paper Prof. LETORT gave a survey of microkinetics and in particular of the theory of the chemical kinetics of homogeneous gas-phase reactions.

The most important quantity in kinetics is the reaction rate. By definition this is the quantity of substance converted per unit time. The reaction rate can be measured by analysing samples taken at certain intervals. Preference should be given, however, to physical methods which enable the course of the reaction to be followed by effecting measurements in the reactor. Although it is not always necessary to know the entire reaction mechanism it is desirable to do so for purely scientific work.

There are simple reactions, which may be mono- bi- or tri-molecular. As a rule they are bimolecular. In addition, there are complex reactions, which may be accompanied by side reactions or consecutive reactions. Besides, chain reactions often occur. They can be classified as processes initiating, propagating or terminating the chain. These reactions are characterized by the fact that one of the links form a particle identical to one that has disappeared before. This was explained by referring to the example of the thermal decomposition of acetic aldehyde, on which Prof. LETORT himself has worked for several years. It is often very difficult to find the mechanism of chain reactions.

The order of a reaction is the sum of the exponents of the concentrations, to which the reaction rate is proportional. Simple mono-, bi- or tri-molecular reactions are first-, second- or third-order reactions. If a reaction proceeds stepwise or is a chain reaction the order is often a fraction. Sometimes the order changes during the reaction under the influence of the products formed.

According to ARRHENIUS, the influence of temperature on the reaction rate is given by the activation energy. This is, so to speak, the energy required to lift the reacting molecules over a potential barrier. In general, the influence of temperature on the reaction rate is considerable. Finally, Prof. LETORT made a few remarks on photochemical reactions.

Prof. KRAMERS gave an introduction to the physical factors playing a part in chemical reaction engineering. First of all he remarked that, for the physicist, it is gratifying to see that physical phenomena greatly assist in making a chemical reaction feasible. Such phenomena include the transportation of reactants and products to and from the reaction zone, the mixing and dispersion, diffusion, heat and mass transfer, which all belong to macrokinetics. They were elucidated in the paper with the aid of some examples worked out by Prof. KRAMERS and his co-workers.

The first two examples had been taken from

the field of hydrodynamics. The first concerned the distribution of residence times in tubular reactors in the case of laminar flow, turbulent flow or flow through a packed bed. The second example showed that in a continuous process with known residence-time distribution it is impossible to calculate the conversion unless the reaction is a first-order one. For reactions of different order the result of the calculation depends on the model chosen to explain the residence time distribution. For actual practice it is a fortunate circumstance that in most cases the differences are not very large.

In the next two examples, which referred to mass transfer, Prof. KRAMERS showed that if a mixture is uniform on the macroscopic scale this need not imply that there is homogeneity on the molecular scale. It is possible to ascertain uniformity, for instance, with the aid of an electric conductivity cell and molecular homogeneity by following the course of a very fast chemical reaction. Another example dealt with mass transfer in a fixed bed. It appears that the data from the literature can be made to fit in with one another over a wide range by applying to the usual correlations some corrections that are easy to justify.

Finally, two examples were given that referred to heat transfer. It was demonstrated that in a fixed bed the ratio of grain diameter to tube diameter may greatly influence the transfer of heat. For a fluidized bed the variables governing heat transfer were divided into two groups: those referring to thermal quantities and those referring to mixing in the bed. The transfer of heat to a small object in the bed, to a low vertical wall and to a high vertical wall must be considered separately.

SECOND SESSION: "TRANSPORT PHENOMENA IN HETEROGENEOUS REACTIONS"

Chairman Prof. Dr. D. W. VAN KREVELEN.

Rapporteur P. J. HOFTIJZER.

Speakers Prof. Dr. E. WICKE (Institut für Physikalische Chemie der Universität Hamburg); Dr. Ir. J. G. VAN DE VUSSE (Koninklijke/Shell-Laboratorium, Amsterdam); Ir. R. A. T. O. NIJSING (Laboratorium voor Fysische Technologie der Technische Hogeschool, Delft); also on behalf of Prof. Ir. H. KRAMERS.

The papers presented at this session all dealt with cases in which the velocity of the process under consideration was dependent, not only on the chemical reaction rate proper, but also on the velocity of a mass transport process. In Prof. WICKE's paper this was the case in heterogeneous gas reactions; the other two papers referred to the absorption of a gas by a liquid, accompanied by a chemical reaction in the liquid.

The title of Prof. WICKE's paper was: "Einfluss des Stofftransportes auf den Verlauf heterogener Gasreaktionen." The discussion of the problem was restricted to isothermal conditions.

First of all the concept of "Verweilzeitprozesse" was defined. They are processes in which the conversion, at constant concentration in the entering gas stream, is only dependent on the average residence time. To them belong all homogeneous isothermic processes in an ideal piston-flow reactor or in an ideal mixer. Heterogeneous processes taking place in these reactors need not be "Verweilzeitprozesse," which is the case, for instance, when a transport phenomenon occurs that is dependent on the gas velocity.

Another definition—given by C. WAGNER—describes the "Abklinglänge," i.e. the length of a tubular reactor in which a fraction $1/e$ of the reacting substance is converted. It is related to the concept of "height of a transfer unit". Equations for the "Abklinglänge" are given for empty tubes as well as for packed beds at laminar and turbulent flow both when transport to the grains and when diffusion in the pores is determinative.

The velocity of a process is generally determined by three factors:

(a) transport to the grains, (b) diffusion in the pores, (c) the reaction proper.

As an example the oxidation of carbon with air in a tube with porous carbon walls was discussed in detail. At temperatures above 1000°C it is the transport in the gas to the tube wall, between

650 and 1000°C the diffusion in the pores and below 650°C the chemical reaction rate that is determinative.

In the discussion Dr. Ir. A. KLINKENBERG objected to the definition of "Verweilzeitprozesse," because actually the process is defined by its change. Prof. WICKE did not agree.

Prof. Ir. H. KRAMERS asked why Prof. WICKE, in his equations, invariably uses the effective thickness of the boundary layer. He himself prefers transfer coefficients. Prof. WICKE considered the preference for either formulation a matter of taste. The use of the effective thickness of the boundary layer, moreover, offers certain advantages from a pedagogical viewpoint.

The other questions asked during the discussion referred to details.

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Dr. VAN DE VUSSE's paper dealt with: "Engineering aspects of the oxidation of mercaptans in caustic solutions. Reaction kinetics and design of reactor." In the process considered the liquid absorbs oxygen from the gas phase, after which the oxidation proceeds in the liquid.

In laboratory experiments it was possible, by applying a high gas velocity and a high stirring speed, to obtain such a rapid transport of oxygen that the reaction rate proper was measured. These kinetic data are used in technical reactor design.

First the reasons for choosing a given type of reactor are given. Under the prevailing conditions the reaction is zero-order for mercaptan and first-order for oxygen. It is, however, easy to supply air in excess. Therefore, the process need not be effected in counter-current and a one-stage stirred reactor will do.

The optimum size of the reactor is considered to be the volume at which the required stirrer energy is minimum. On the volume being increased the reaction may proceed at a lower concentration of oxygen in the liquid, so that a lower coefficient of mass transport is required. At a given certain excess of oxygen, however, the "superficial gas velocity" also drops when volume is increased, which means that the stirrer speed must be raised to attain the transfer coefficient desired. The magnitude of the transfer coefficient under given conditions of stirring is taken from the literature.

The calculations lead to an optimum reactor volume, at which the stirrer energy is minimum. The concentration of dissolved oxygen is then about one-third of the saturation concentration.

In the discussion Dr. KLINKENBERG drew attention to the agreement between the equations for absorption attended by chemical reaction (HATTA) and the equations for pore diffusion (WICKE).

Ir. NIJSING objected to the rate of physical mass transport being calculated from the measuring results of COOPER, FERNSTROM and MILLER. These investigators measured the absorption of oxygen in sulphite solutions, hence, again an absorption with chemical reaction. In Dr. VAN DE VUSSE's opinion, however, in this case the physical rate of transport was measured all the same.

Drs. TH. N. ZWIETERING remarked that in the optimum situation described by Dr. VAN DE VUSSE the gas velocity is very low. From an economical viewpoint it is probably more profitable to operate at a higher gas velocity, which enables the stirrer energy to be reduced considerably.

Several discussers asked for further information on numerical quantities used and on the derivation of the formulae.

The paper of Ir. NIJSING and Prof. KRAMERS entitled: "Absorption of CO_2 in carbonate–bicarbonate buffer solutions in a wetted-wall column" was presented by Ir. NIJSING.

Experiments had been made under conditions at which the penetration theory is valid. This means that the substance to be absorbed penetrates into the liquid at the same rate as with diffusion into a semi-infinite medium, during a time which is equal to the quotient of column height and superficial liquid velocity. As the concentrations of carbonate and bicarbonate ions remain practically constant the concentration of OH^- ions is also constant. Thus, it is allowed to apply DANCKWERTS' equations to the combination of diffusion and a first-order reaction.

The extent to which the conditions made were satisfied in the experiments was ascertained in

detail. The only important correction taken into consideration was an " end effect".

In applying the theoretical relation for the rate of absorption to the experimental data two unknown quantities must be taken into account, viz. (a) the solubility of CO_2 in the absorption liquid, which determines the CO_2 concentration at the liquid surface, and (b) the reaction rate. Both quantities can be deduced from the experimental data. They are both functions of the liquid composition. There is good agreement with literature data.

In the discussion the concept of " penetration theory " was brought up. The definition of NIJSING and KRAMERS was given above. In Dr. VAN DE VUSSE's opinion, however, this name is better reserved for the picture suggested by DANCKWERTS, in which turbulence "penetrates" as far as the phase boundary.

THIRD SESSION : " NON-UNIFORM CONCENTRATION DISTRIBUTIONS "

Chairman Prof. Ir. H. KRAMERS.

Rapporteur Ir. TH. W. WILLEMSE.

Speakers Prof. Dr. P. V. DANCKWERTS (Imperial College of Science and Technology, London) ; Dr. K. RIETEMA (Koninklijke/Shell – Laboratorium, Amsterdam) ; Dr. H. HOFMANN (Institut für Chemische Technologie, Technische Hochschule, Darmstadt).

This session dealt with reactions taking place in heterogeneous or seemingly homogeneous systems, in which the interaction between non-homogeneity on the one hand and conversion and yield on the other play an important part.

In Prof. DANCKWERTS' paper : " The effect of incomplete mixing on homogeneous reactions " the flow behaviour of the reactants in a continuous reactor was discussed. For a homogeneous first-order or pseudo-first-order reaction it is sufficient to know the residence-time distribution to enable the initial composition to be calculated, because the chance of a molecule reacting is exclusively dependent on the duration of its stay in the reactor. In the case of reactions with more complex kinetics the chance of a molecule reacting depends on the number of molecules it encounters during its stay, so that a great deal more information is required. Complete calculation is then only possible in a few special cases, e.g. the tubular reactor with longitudinal diffusion.

A method of approach to the general problem was suggested. Two extreme cases that can be calculated from the residence-time distribution can be distinguished :

(a) The incoming liquid is broken up into discrete fragments which are small compared to the reactor and in which molecules entering together remain together : complete segregation. Model : ideal tubular reactors arranged in parallel. Special case : the " well-stirred " tank reactor without molecular diffusion.

(b) The reactants are dispersed on the molecular scale in a time which is small compared to the average residence time : the perfect mixer with homogeneous mixing on the molecular scale.

If the reaction mixture consists of two reactant streams the average reaction rate will, in general, depend on the ratio between these two extremes, hence, on the " degree of segregation". It was demonstrated that mixing on the molecular scale between elements of fluid having different ages reduces the conversion if the order of the reaction is higher than 1 and causes it to increase when this order is lower than 1.

A quantitative definition of the degree of segregation was given for a two-component system and for the elements of different ages of a liquid stream passing a reactor. The requisite specification of the size of the areas of inhomogeneity was obtained by defining a " scale of segregation " with the aid of a technique known from the statistical turbulence theory.

The degree of segregation can be measured with the aid of slow reactions. In actual practice the study of segregation phenomena will probably be most useful for very fast reactions, such as combustion or precipitation. A few examples were given.

In the discussion it was pointed out that in

many cases the conversion can be calculated, with an accuracy sufficient for practice, from the residence-time distribution on the basis of complete segregation, viz. for slow reactions of an order between ½ and 2 if the residence-time distribution more or less corresponds to that of a cascade consisting of more than one ideal mixer.

On the other hand, with many slow reactions occurring in stirred vessels it will be easy to reach such a degree of mixing that one is sure to obtain homogeneity.

A reaction is " slow " in the sense meant here and a study of segregation is thus of little importance if the relaxation time for the reaction between the substance in the areas of inhomogeneity and the surrounding liquid is much longer with homogeneous mixing than the relaxation time for the dispersion of these areas by diffusion.

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Dr. RIETEMA presented a paper entitled : " Heterogeneous reactions in the liquid phase. Influence of residence-time distribution and interaction in the dispersed phase." He discussed the development of heterogeneous reactions in the liquid phase in continuous reactors for cases in which the average residence times of the two phase do not differ much because the dispersion is maintained by turbulence and entrainment occurs. In these cases it is possible to carry out representative experiments in batch and, on the strength of their results, to predict the course of the reaction in the continuous reactor.

If the reaction takes place in the continuous phase the reaction can be regarded as a homogeneous one and hence be treated with the graphical methods known for the purpose. This can also be done when the reaction occurs in the dispersed phase or in the boundary layer around this phase, provided the exchange in the disperse phase is so fast that all the particles of this phase invariably have the same composition. This is possible, for instance, for reactions between two liquids, the exchange being effected by continuous coalescence and redispersion of the disperse phase.

For the opposite phase, e.g. in a solid – liquid system, a new graphical method was suggested and worked out for a reaction in an ideal mixer, in which—in DANCKWERTS' terminology—the continuous phase is mixed on the molecular scale and complete segregation takes place in the disperse phase. In the latter a distribution of the degree of conversion is brought about which corresponds to the residence-time distribution, the conversion in the continuous phase being the same throughout.

Essentially, the method consists in the graphical determination of reaction rates, at a given concentration in the continuous phase and at various concentrations of the disperse phase, from the results of a series of experiments with different concentrations of the continuous phase.

Complications arise with liquid – liquid reactions. They are caused by a difference in degree of dispersion between batch and continuous reactions and by an exchange to an unknown degree in the disperse phase. In accordance with DANCKWERTS' theory it was calculated for a zero-order reaction (mass transfer fully determinative) that at 80 per cent conversion through complete mixing of the disperse phase the reactor volume can be reduced by a factor of 3.

The influence of surface-active substances and contaminations is so complicated that exact predicting of the conversion for liquid – liquid reactions will probably never be possible. In the discussion it was mainly the behaviour of liquid – liquid dispersions and the way in which they can be obtained that were brought up.

Dr. HOFMAN, in his paper : " Berechnung von Reaktoren für Gemischtphase-Reaktionen", dealt with the chemical reactions which proceed to completion as homogeneous reactions in one or several phases, it being supposed that these phases are homogeneous or, through exchange, can be considered homogeneous.

In many technically important reactions in the liquid phase, such as nitrations and sulphations, the reactants are intersoluble to only a limited degree, so that the conversion takes place in two (or more) phases. Consequently, the conversion is also dependent on the solubility and the rate of dissolving of the reactants in the reacting phase(s).

An analogous case occurs when in a reaction in a homogeneous phase e.g. with an undesirable

consecutive reaction the conversion is increased by separating the product, for instance, by extraction, distillation or crystallization.

In general, the rate of conversion will be determined by both the mass transfer and the chemical reaction. By introducing the " mixing yield " (HOUGEN), i.e. the ratio of the conversion rate actually attained to the rate of conversion at ideal mixing (phase equilibrium) all cases can be reduced to a single one in which the chemical reaction is fully determinative. In this case, use is made of a " distribution value " (SCHOENEMANN), i.e. the reciprocal value of the fraction of a substance in one of the phases.

With the aid of material balances the conversion was calculated for a number of idealized apparatus, in particular also for the countercurrent case, technically interesting reactions serving as quantitative models.

With the example of the production of furfural from an aqueous xylose solution containing hydrochloric acid it was demonstrated that it is possible to predict the optimum shape and size of the reactor also in complicated technical cases, provided the reaction rate equation is known.

In accordance with the many degrees of freedom : ratio between phase quantities, distribution coefficient, concurrent or countercurrent operation, etc. there are a great many possibilities for effecting one and the same reaction, the optimum choice from which can only be made by checking the various possibilities through quantitative calculation. The non-linearity of the equations in case the reaction is not a first-order one in general calls for the use of a computer.

In the discussion a problem with a second-order reaction was given which is comparatively easy to solve.

FOURTH SESSION : " REACTOR EFFICIENCY AND STABILITY "

Chairman Dr. Ir. A. KLINKENBERG.

Rapporteur Ir. W. J. VAN ASSELT.

Speakers Prof. Dr. K. G. DENBIGH (University of Edinburgh and Heriot-Wall College) ; Dr. C. VAN HEERDEN (Central Laboratorium, Staatsmijnen in Limburg) ; Dr. Ir. A. P. OELE (Chemiebouw, Staatsmijnen in Limburg).

In this session the attention was devoted particularly to the interaction between the temperature and its gradient in chemical reactors and reactor efficiency and stability.

The following cases were discussed :

(a) Influence of temperature on the conversion per unit time and per unit volume with simple reversible reactions.

(b) Influence of temperature in consecutive and simultaneous reactions. In this case a different temperature may result in a different yield.

(c) Influence of temperature on reactor stability.

Prof. DENBIGH, in his paper entitled : " Optimum temperature sequences in reactors", discussed cases (a) and (b).

In an equilibrium reaction with a positive heat effect an increase in temperature will increase the reaction rate but also shift the equilibrium towards a lower conversion. A decrease in temperature along the length of the reactor will, in this case, cause the conversion to increase and it is comparatively easy to calculate the optimum temperature profile. The influence of temperature on the yield of consecutive and simultaneous reactions was discussed in more detail.

When the activation energies of main and side reactions are different the reaction can be influenced in a certain direction by changing the temperature. With the aid of a numerical example it was demonstrated that in a given case the yield of a reaction in a two-tank cascade can be doubled by keeping the two reactors at different temperatures.

Of course these optimum values for the temperatures in the two reactors are also optimum values from an economical viewpoint only when the economy is completely determined by the consumption of starting material and, accordingly, the capital and operating costs play a minor role.

Hence, it is possible to find an optimum temperature for every continuous reactor in which there is a given concentration of reactants and intermediate products. It is thus to be

expected that in a tubular reactor, in which the temperature can be controlled at any point, the yield can possibly be increased by continuous variation of the temperature over the length of the reactor. In the discussion Dr. F. HORN went further into this point.

In the above considerations on conversion and yield the heat effect of the reaction was left out of account. In his paper, Dr. VAN HEERDEN considered mainly those exothermic reactions in which the reaction heat itself is wholly or largely used to heat the reactants up to reaction temperature (autothermic processes).

In a technical continuous reactor there will be, at every temperature, a certain conversion and hence a certain quantity of heat will be liberated. Plotting this heat against the prevailing temperature results in an S-curve whose first part (like the reaction rate) practically runs according to an e-power function. Afterwards, however, the curve is bent to a constant value of the heat produced, which corresponds to complete conversion. On the other hand the heat required for heating the reaction mixture to the final temperature, plotted as a function of this temperature, is represented by a straight line.

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For an autothermic reaction to be realized both relations must be satisfied at the same time.

In order to describe the solutions of the two relations Dr. VAN HEERDEN uses the quantities T_e and ΔT_{ad}, defined as follows :

T_e is the temperature at which a conversion $1/e$ is obtained at isothermic piston-flow through a reactor with known residence time. (At this temperature, therefore, the reactor length is exactly the "Abklinglänge".)

ΔT_{ad} is the adiabatic rise in temperature of the reaction mixture at complete conversion.

If the reaction is carried out in an ideal mixer the following cases can be distinguished :

(a) T_0 (starting temperature) $+ \Delta T_{ad} < T_e$. In this case the curves have only one point of intersection, viz. at low conversion. This reaction, therefore, cannot be effected in an ideal mixer without special measures.

(b) $T_0 + \Delta T_{ad} \sim T_e$. The curves have three points of intersection, two of which are stable. After ignition of the reaction a stationary state establishes itself at a point of high conversion and at high temperature.

(c) $T_0 + \Delta T_{ad} > T_e$. This results in complete conversion at a very high temperature.

The reaction mentioned under (a) can be effected in a tubular reactor with heat exchange between inlet and outlet. Thus, T_0 is increased to T_0' and $T_0' + \Delta T_{ad} \sim T_e$.

Finally, Dr. VAN HEERDEN considered piston flow with axial heat conduction, characterized by Péclet's number (Pé $= \rho v\, c_p L/\lambda$). If Pé $\ll 1$ there is hardly any difference in temperature between inlet and outlet and one has an approximation to the case of an ideal mixer with three stationary states (two of them stable). In the other extreme, Pé $\ll 1$, there is only one stationary state.

Whereas in the subject dealt with by Dr. VAN HEERDEN and Prof. DENBIGH temperature plays an important role in connexion with the reaction velocity. Dr. OELE discussed a reaction in which the temperature is so high that mass transfer determines the overall rate. In this example ammonia and air (8–11 per cent NH_3) are passed over a few layers of platinum wire gauze at about 800°C. The heat liberated during the oxidation corresponds to the increase in sensible heat in reaction products and inert gases.

The theoretical analogy between heat transfer (U) and mass transfer (α) can be written by :

$$\alpha/U = 1{\cdot}03\, C_p^{-1}\, P^{-1},$$

(where C_p = specific heat at constant pressure per kmol of gas mixture,

P = pressure of gas mixture)

and it is easy to deduce that in this case the temperature of all platinum wire gauzes is practically equal to $T_0 + \Delta T_{ad}$.

When, however, the gauzes have been in use for some time a retardation of the reaction occurs,

to be represented by the retardation factor i, which from 0·8 to 1.

$$\alpha'/U = i\, C_p^{-1}\, P^{-1}.$$

The temperature of the gauzes then rises in the direction of flow. Besides, this factor i is very important for burner stability. For, on the gas throughput being increased and if $i < 1$, U will increase more than α', since α' is composed of α and the reaction rate, of which only α increases. In this case, therefore, the gauzes may be blown cold. Consequently, to eliminate the influence of the reaction rate it is necessary, dependent on catalyst activity, to preheat the gases so as to obtain stable oxidation.

Since i results from deactivation of the catalyst, at $i < 1$ preheating should be carried further. In addition, a temperature gradient appears in the gauzes, which may lead to impermissible platinum losses.

FIFTH SESSION : "REACTOR DEVELOPMENT"

Chairman Prof. Dr. Ir. H. I. WATERMAN.

Rapporteur Dr. Ir. C. BOELHOUWER.

Speakers Prof. Dr. K. SCHOENEMANN (Technische Hochschule, Darmstadt); Dr. F. SCHNUR (Ruhrchemie Aktiengesellschaft, Oberhausen-Holten), also on behalf of Dr. W. BRÖTZ (Th. Goldschmidt Aktiengesellschaft, Mannheim-Rheinau); Dr. Ir. A. KLINKENBERG (N.V. De Bataafsche Petroleum Maatschappij, The Hague).

Prof. SCHOENEMANN discussed "Die Anwendung der Reaktionskinetik bei der Berechnung einiger typischer Reaktoren".

In the light of a number of examples taken from actual practice the importance of kinetic calculations for the development of chemical processes from the laboratory stage up to large-scale technical application was demonstrated. It is particularly the development of the high-pressure hydrogenation processes for coal and oil that has greatly contributed towards a clearer formulation of the problems involved. A better understanding was gained of simple basic concepts, such as residence time distribution in continuous processes and its importance for the computation of type, shape and size of the reactors.

The course of homogeneous and pseudo-homogeneous reactions in the most widely divergent types of continuous reactors can be calculated if the residence time distribution and the reaction rate are known; for reactions in more than one phase often the requisite experimental data are lacking, particularly those concerning mass transfer.

As an example of a complicated chemical reaction the preparation of the explosive hexogene [*cyclo*trimethylenetrinitramine, $(CH_2)_3\,N_3\,(NO_2)_3$] by nitration of hexamethylene tetramine was discussed. When through careful laboratory experiments a quantitative picture of the various conversions playing a part in this nitration had been obtained it was found possible to design at once, without an intermediate stage, a continuous technical plant which worked satisfactorily.

In exothermic high-pressure processes often a circulation system is used to remove the reaction heat. Admittedly, this system leads to a much lower production per unit of volume and time, but it is necessary in order to be able to control the temperature in the reactor. This empirically developed method, which is in general use, can now be quantitatively computed in various cases, as was illustrated by a diagram for the synthesis of 1 : 4-butyndiol from acetylene and formaldehyde with the aid of an acetylene-copper catalyst.

In addition, the hydrolysis of wood according to Madison's method—as an example of a percolation process—was discussed as well as the production of furfural from vegetable material containing pentosanes, where the yield is strongly influenced by condensation and resinification of the desired product under the influence of the acid used for the hydrolysis of the pentosanes.

Prof. SCHOENEMANN came to the conclusion that application of reaction kinetics in the calculation of technical reactors has often provided useful data. If these are correctly combined with other factors determinative of an exploitation that is economically justified, such as choice of material (also with regard to safety), heat economy, power consumption, etc. it is

possible to arrive at a more rational development and design of chemical works.

In the discussion Dr. KLINKENBERG went further into the reaction mechanism of the hexamethylenetetramine nitration. Prof. WATERMAN drew attention to recent investigations carried out by WEBER at Delf on the characterization of catalysts with the aid of simple hyperbolic functions.

Dr. SCHNUR presented, also on behalf of Dr. BRÖTZ, their paper: "Verfahrensmässige Berechnungen des Stoffaustausches gelegentlich der Absorption von Stickstoffoxyden bei der Gewinnung von Salpetersäure".

The rate of absorption of nitrous gases, which is important in nitric acid manufacture, was studied on the basis of measurements taken on a laboratory scale in a thin-film absorber, in a semi-technical packed column, and on a technical scale in a nitric acid factory. The influence of various factors on the rate of absorption was studied in order to arrive at an empirical relation for the mass transfer coefficient k_g. The considerations were based on the two-film concept. Laboratory-scale experiments showed that, in accordance with earlier observations of CHAMBERS and SHERWOOD, the diffusion resistance of the liquid could be neglected in respect of that of the gas film.

In the semi-technical absorption column filled with Raschig rings the mass transfer coefficient was found to be dependent on the liquid throughput if the latter was low; above a certain throughput the mass transfer coefficient was independent of it if the packing is wetted completely. In accordance with the theory no influence of the diameter of the Raschig was found. The way of packing (rings placed or poured into the column) did have an influence, though.

Although the measurements made in the technical plant were of somewhat limited accuracy it was clear that the mass transfer coefficient dropped with decreasing concentration of both gas and acid, contrary to what was to be expected on the strength of the laboratory-scale experiments in the thin-film absorber.

From the observations it might be concluded that the conversion proper of the nitrous gases with water vapour occurs in the gas phase, preferably in the immediate vicinity of the phase boundary.

Messrs. HOFTIJZER, NIJSING, DEKKER and Prof. VAN KREVELEN took part in the discussion. Among other things, the difficulties that may arise in the interpretation of the measuring results on account of mist formation were brought up.

In his final remarks on the symposium Dr. KLINKENBERG tried to arrive at a systematic survey of the field of chemical reaction engineering in the light of the various papers presented.

Formerly, in dealing with chemical engineering use was often made of a classification according to the so-called unit operations and unit processes. This symposium revealed a strong desire to go back to the fundamental concepts. They are as follows:

Equilibria	*Rates*
Thermodynamics (including phase equilibria)	Fluid dynamics Heat transport Mass transport
Chemical equilibria	Reaction kinetics (simple reactions) Reaction kinetics (side reactions, consecutive reactions, etc.)

Chemical reaction engineering is not concerned with the chemistry of the reaction. Those chemical reactions should be classified together which (even though they are entirely different from a chemical viewpoint) are analogous as far as certain physical and physico-chemical criteria are concerned and which can be operated in the same type of reactor.

The study of chemical reaction engineering is more difficult than the study of processes in which chemical conversion does not occur (the unit operations). In addition to the fundamental concepts of flow, heat and mass transport, which moreover are often strongly interdependent in in this case, we have also to deal with chemical reaction. Chemical reaction engineering is more than a combination of unit operations and chemistry, as the Symposium Committee tried to express in the syllabus.

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To simplify the treatment of chemical reaction engineering problems various methods can be applied :

(a) Separation into equilibria and rates (or, if necessary, restriction to equilibria) ; (b) restriction to flow and reaction kinetics (e.g. isothermic homogeneous reactions in stirred vessels) ; side and consecutive reactions may be included ; (c) disregard of the reaction rate in respect of the rate of transfer, or conversely ; (d) use of statistical considerations to simplify the treatment of steps that repeat themselves ; (e) use of differential reactors.

This was explained by referring to the various communications made at the Symposium.

The theory of uniformity, too, is an important tool ; it tries to find new solutions on the basis of other solutions already known.

However, in classifying and subdividing the subjects belonging to chemical reaction engineering oversimplification in formulating the problems should be avoided.

Dr. BRETSCHNEIDER spoke a few words on behalf of the European Federation for Chemical Engineering to thank the Symposium Committee and particularly its Chairman, Dr. Ir. J. C. VLUGTER, for the considerable amount of important work that had been done to enable this twelfth meeting of the Federation.

The closing words were spoken by Dr. D. J. GERRITSEN as Chairman of the Chemical Engineering Section of the Royal Institute of Engineers. Dr. GERRITSEN, on behalf of the two organizing societies, also tendered his thanks to all those that had taken part in the organization. He stressed that symposia of this nature are not only scientific meetings but also manifestations of a European collaboration which we all need so much nowadays. In this connexion Dr. GERRITSEN recalled the words spoken by Prof. LETORT at the reception by the Burgomaster of Amsterdam that the Netherlands have always stood in the breach for freedom of thought and speech.

Dr. GERRITSEN then declared the Symposium closed.

On the evening of the first day the participants were received by the Burgomaster of Amsterdam in the stylish surroundings of the Municipal Museum. On the last day the organizing societies invited them to a cocktail party, where the lively exchange of ideas was continued.

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Notes on the diffusion-type model for the longitudinal mixing in flow (O. Lievenspiel and W. K. Smith)*

(*Received* 17 *September* 1957)

In their article (referred to below as "article") the authors use the diffusion type approach to characterize the longitudinal mixing of fluids in flow. Two methods are shown for evaluating the diffusion coefficient D. In the first method either the maximum concentration or the concentration at $v\vartheta/V = 1$ (notation article and here) is measured. In the second method the concept of the variance of the concentration distribution σ^2 is introduced. The article is restricted to the treatment of the infinite pipe: one value of D applies to the entire length and cross-section.

It is the object of this letter to treat the diffusional type of flow in a more general manner so as to include the case of finite pipe length and that of varying D, applying suitable boundary conditions. For a discussion of the boundary conditions chosen we refer to an article by Wehner and Wilhelm [1].

It will be shown that for the case of small D/UL† the influence of the special end effects can be ignored. The question whether the description of the mixing phenomena by using the mathematics of diffusion in the case of large D is still permissible will not be discussed.

Futhermore it is shown that for the case where the average flow velocity u is known it is in some cases not necessary to compute the variance, as the computation of the mean time of passage of the tracer material leads to an evaluation of the diffusion coefficient D.

In the solution use is made of the Laplace transform. This has the advantage of transforming the partial differential diffusion equation into an ordinary linear differential equation, the solution of which is simple. To derive expressions for the variance, etc. it is not necessary to perform the (cumbersome) back transformation.

The differential equations

A finite pipe of length L is bounded at both sides by a fore- and after-section (sections a and b resp.). As with Wehner and Wilhelm [1] these two end sections stretch from $-\infty$ to $+\infty$. In the fore- and after-section different values for the diffusion coefficients compared with the value in the finite tube (D) occur. These are designated by D_a, D_b resp. (Fig. 1). Injection of tracer material at a distance x_0 downstream of the entrance of the finite tube is supposed to take place so rapidly, without interfering with general flow, that this introduction into the flow can be mathematically described by the Dirac δ-function.

Introduction of reduced quantities and variables (see notation) leads to the following set of differential equations

$$\left(\frac{\partial}{\partial\vartheta} + \frac{\partial}{\partial z} - \frac{1}{Pe_a}\frac{\partial^2}{\partial z^2}\right)R_a = 0 \qquad z \leqq 0 \qquad (1a)$$

$$\left(\frac{\partial}{\partial\vartheta} + \frac{\partial}{\partial z} - \frac{1}{Pe}\frac{\partial^2}{\partial z^2}\right)R = \delta(\vartheta)\,\delta(z - z_0) \quad 0 \leqq z \leqq z_1 \qquad (1b)$$

$$\left(\frac{\partial}{\partial\vartheta} + \frac{\overline{\partial}}{\partial z} - \frac{1}{Pe_b}\frac{\partial^2}{\partial z^2}\right)R_b = 0 \qquad z \geqq z_1 \qquad (1c)$$

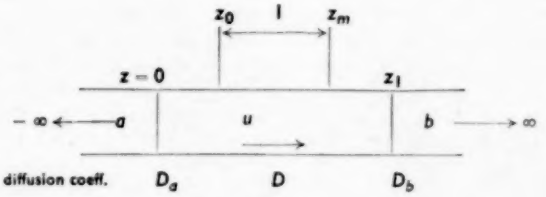

Fig. 1.

The function R equals CV/Q. It is a kind of dimensionless residence time distribution. For locations downstream of the injection point it can be proved that (equation (10))

$$\int_0^\infty R\,d\vartheta = 1 \qquad z \geqq z_0 \qquad (2)$$

Boundary conditions

In order to solve equations (1a – 1c), apart from the obvious initial conditions $\vartheta < 0$; $R_a = R_b = R = 0$, six boundary conditions are needed. Two conditions follow immediately from the consideration that at $z = +\infty$ R_a and R_b must remain finite (3a, 3b).

From the law of conservation of material at the boundaries there ensue two other equations (3c, 3d).

The other two boundary equations (3e, 3f) arise from the intuitive argument that between the sections at the pipe entrance and exit the concentrations should be continous (see also [1]).

So the complete set of boundary equations is:

$$R_a(-\infty) = \text{finite} \qquad (3a)$$

* Article published in *Chem. Engng. Sci.* 1957 **6** 227.

† Here L is used as the length of the experimental section as contrasted with length of the finite tube in the rest of letter.

$$R_b(+\infty) = \text{finite} \tag{3b}$$

$$R_a(0^-) - \frac{1}{Pe_a}\frac{dR_a(0^-)}{dz} = R(0^+) - \frac{1}{Pe}\frac{dR(0^+)}{dz} \tag{3c}$$

$$R(z_1-) - \frac{1}{Pe}\frac{dR(z_1^-)}{dz} = R_b(z_1^+) - \frac{1}{Pe_b}\frac{dR(z_1^+)}{dz} \tag{3d}$$

$$R_a(0^-) = R(0^+) \tag{3e}$$

$$R(z_1^-) = R_b(z_1^+) \tag{3f}$$

Properties of the Laplace transform of R

It is convenient to introduce the Laplace transform of R in the form

$$\overline{R}(p) = \int_0^\infty e^{-p\vartheta}\, R(\vartheta)\, d\vartheta \tag{4}$$

Introduction of $\overline{R}$ stems from the consideration that Laplace transformation of the partial differential equations (1a → 1c) and solving the ensuing linear ordinary differential equations, taking into account the boundary conditions (3a → 3f), leads to the solution of $\overline{R}$ as a function of z and p. To obtain the value for the variance σ^2 it is not necessary to perform the cumbersome back transformation of $\overline{R}(p)$. This can be visualized by taking the first two derivatives of $\overline{R}$ with respect to p and going to the limit $p \to 0$:

$$-\left(\frac{d\overline{R}}{dp}\right)_{p\to 0} = \int_0^\infty \vartheta\, R d\,\vartheta = \overline{\vartheta} \tag{5}$$

$$\left(\frac{d^2\overline{R}}{dp^2}\right)_{p\to 0} - \left(\frac{d\overline{R}}{dp}\right)^2_{p\to 0} = \int_0^\infty \vartheta^2\, R d\,\vartheta - \overline{\vartheta}^2 = \sigma^2 \tag{6}$$

Equation (6), taking into account equation (5) is similar to equation (10) of article.

General solution of $\overline{R}$ (p)

Taking the Laplace transform of the partial differential equations (1a) → (1c), solving the ordinary linear differential equations in $\overline{R}(p, z)$, taking into account the boundary conditions (3a) → (3f) gives

$$\overline{R}_a = A e^{(q_a + \frac{1}{2})Pe_a z} \qquad z \leqq 0 \tag{7a}$$

$$\overline{R} = \frac{A}{2q}\left[(q+q_a)\, e^{(q+\frac{1}{2})Pez} + (q-q_a)\, e^{-(q-\frac{1}{2})Pez}\right] - \frac{U(z-z_0)}{2q}\left[e^{(q+\frac{1}{2})Pe(z-z_0)} - e^{-(q-\frac{1}{2})Pe(z-z_0)}\right]$$
$$0 \leqq z \leqq z_1 \tag{7b}$$

$$\overline{R}_b = B\, e^{-(q_b-\frac{1}{2})Pe_b(z-z_1)} \qquad z \geqq z_1 \tag{7c}$$

where A and B are :

$$A = e^{-\frac{1}{2}Pez_0}\, \frac{(q+q_b)\, e^{qPe(z_1-z_0)} + (q-q_b)\, e^{-qPe(z_1-z_0)}}{(q+q_a)(q+q_b)\, e^{qPez_1} - (q-q_a)(q-q_b)\, e^{-qPez_1}} \tag{8a}$$

$$B = \overline{R}(z \to z_1) \tag{8b}$$

The solution for z_m $(z_0 < z_m \leqq z_1)$ is the one required :

$$\left.\begin{aligned}\overline{R}(p, z_m) = {} & \frac{e^{-(q-\frac{1}{2})Pe}}{2q} \times \\ & \times \frac{(q+q_a)(q+q_b) + (q-q_a)(q-q_b)}{e^{-2qPe(z-1-1)} + (q-q_a)(q+q_b)\, e^{-2qPez_0}} \\ & \overline{(q+q_a)(q+q_b) - (q-q_a)(q_{,}-q_b)\, e^{-2qPez_1}} \\ & \times \frac{(q-q_a)(q+q_b) \times e^{-2qPe(z_1-z_m}}{}\end{aligned}\right\} \tag{9}$$

It is interesting to calculate $\overline{R}(p \to 0)$ as this gives the fraction of injected material which passed the location z. From (4) and (7a → 8b) we find (2)

$$\left.\begin{aligned}\overline{R}(p \to 0) = \int_0^\infty R d\,\vartheta = 1 \qquad & \text{for } z \geqq z_0 \\ e^{-Pe(z_0-z)} \qquad & \text{for } 0 \leqq z \leqq z_0 \\ e^{-(Pez_0 - Pe_a z)} \qquad & \text{for } z \leqq 0\end{aligned}\right\} \tag{10}$$

Calculation of $\overline{\vartheta}$ and σ^2 (Table 1)

Applications of (5) and (6) to (9) leads in a straight forward way to values for $\overline{\vartheta}$ and σ^2. The general solution (case I) and some special cases are listed in Table 1. Note that for large values of Pe the general solutions of $\overline{\vartheta}$ and σ^2 tend to the following values :

$$\overline{\vartheta} \to 1 \quad \text{for } Pe \to \infty \tag{11a}$$

$$\sigma^2 \to 2/Pe \text{ for } Pe \to \infty \tag{11b}$$

Equation (11b) corresponds to equation (14) of article. The special cases were derived from the following considerations

tube from $x = 0 \to \infty$ take values of b section equal to finite tube or $Pe_b = Pe$

tube from $-\infty \to x = 1$ take $Pe_a = Pe$

tube from $-\infty \to +\infty$ $Pe_a = Pe = Pe_b$

no diffusion in sections a and b $Pe_a = Pe_b = \infty$

The special case treated in article is case VII of Table 1. The variance σ^2 in this case equals equation (12) from article.

Calculations of $\overline{\vartheta}$ and σ^2 from the F-curve

Article introduced the F-curve as the output for a step function. It can be shown that this output is related to the R-curve in the following way (see also [2]).

$$F(\vartheta) = \int_0^\vartheta R d\,\vartheta \tag{12}$$

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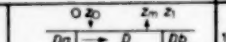
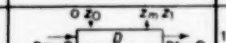
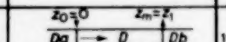
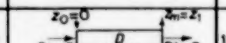
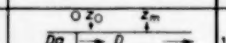
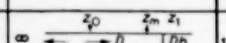
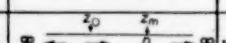
***Table* 1**

		$\bar{\theta}$	σ^2
I		$1+\frac{1}{Pe}\left[2-(1-\alpha)e^{-Pez_0}-(1-\beta)e^{-Pe(z_1-z_m)}\right]$	$\frac{1}{Pe^2}\left[2Pe+8+2(1-\alpha)(1-\beta)e^{-Pez_1}-(1-\alpha)e^{-Pez_0}\left\{4z_0Pe+4(1+\alpha)+(1-\alpha)e^{Pez_0}\right\}-(1-\beta)e^{-Pe(z_1-z_m)}\left\{4(z_1-z_m)Pe+4(1+\beta)+(1-\beta)e^{Pe(z_1-z_m)}\right\}\right]$
II		$1+\frac{1}{Pe}\left[2-e^{Pez_0}-e^{Pe(z_1-z_m)}\right]$	$\frac{1}{Pe^2}\left[2Pe+8+2e^{Pez_1}-e^{Pez_0}\left\{4z_0Pe+4+e^{Pez_0}\right\}-e^{Pe(z_1-z_m)}\left\{4(z_1-z_m)Pe+4+e^{Pe(z_1-z_m)}\right\}\right]$
III		$1+\frac{1}{Pe}\left[\alpha+\beta\right]$	$\frac{1}{Pe^2}\left[2Pe-2+2e^{Pe}+2(\alpha+\beta)(1-e^{Pe})+3(\alpha^2+\beta^2)+2\alpha\beta e^{Pe}\right]$
IV		1	$\frac{2}{Pe^2}\left[Pe-1+e^{Pe}\right]$
V		$1+\frac{1}{Pe}\left[2-(1-\alpha)e^{Pez_0}\right]$	$\frac{1}{Pe^2}\left[2Pe+8-(1-\alpha)e^{Pez_0}\left\{4z_0Pe+4(1+\alpha)+(1-\alpha)e^{Pez_0}\right\}\right]$
VI		$1+\frac{1}{Pe}\left[2-(1-\beta)e^{Pe(z_1-z_m)}\right]$	$\frac{1}{Pe^2}\left[2Pe+8-(1-\beta)e^{Pe(z_1-z_m)}\left\{4(z_1-z_m)Pe+4(1+\beta)+(1-\alpha)e^{Pe(z_1-z_m)}\right\}\right]$
VII		$1+\frac{2}{Pe}$	$\frac{1}{Pe^2}\left[2Pe+8\right]$
VIII		$1+\frac{1}{Pe}$	$\frac{1}{Pe^2}\left[2Pe+3\right]$

$Pe=\frac{U(x_m-x_0)}{D}$ $\quad\alpha=\frac{Da}{D}$

$z=\frac{x}{x_m-x_0}$ $\quad\beta=\frac{Db}{D}$

or making use of a well known relation of Laplace transforms :

$$\overline{F} = \overline{R}/p \tag{12a}$$

Introduction of the function

$$f(\vartheta) = 1 - F(\vartheta) \tag{13}$$

and

$$\overline{f} = \frac{1}{p} - \overline{F} \tag{13a}$$

into equation (12a) with subsequent application of (5) and (6) leads to the relations

$$\overline{\vartheta} = \int_0^\infty (1 - F(\vartheta))\, d\,\vartheta \tag{14}$$

$$\sigma^2 = 2\int_0^\infty \vartheta\,(1 - F(\vartheta))\, d\vartheta - \overline{\vartheta}^2 \tag{15}$$

Determination of the diffusion coefficient

In those cases where $D_a = D_b = 0$ or D the equations of Table 1 may be used for the evaluation of the diffusion coefficient D. For small values of the Peclet number Pe it is sufficient in many cases to have experimental information on $\overline{\vartheta}$ only. From the definition of $\overline{\vartheta}$ and σ^2 there follows with $V/v = (x_m - x_0)/u$ the mean residence time of the fluid in the experimental section, and C some concentration of the tracer, which in this case need not be dimensionless :

$$\overline{\vartheta}\,(V/v) = \frac{\int_0^\infty \theta C d\theta}{\int_0^\infty C d\,\theta} = \overline{\theta} \tag{16}$$

$$\sigma^2\,(V/v)^2 = \frac{\int_0^\infty \theta^2\, C d\,\theta}{\int_0^\infty C d\,\theta} - \left\{\frac{\int_0^\infty \theta\, C d\,\theta}{\int_0^\infty C d\,\theta}\right\}^2 = s_\theta{}^2 \tag{17}$$

The right hand side can be calulated from the measured C-curve. Furthermore $\overline{\vartheta}$ and σ^2 are known functions of the Peclet number (Table 1). Two cases may arise :

Case (a) : V/v is known. Now it is possible to calculate $\overline{\vartheta}$ immediately from (16) : $\overline{\vartheta} = \overline{\theta}/(V/v)$. From Table I $\overline{\vartheta}$ is a known function of Pe, which value can be calculated. Calculation of σ^2 by way of Table 1 and comparing this value with $s_\theta{}^2\,(v/V)^2$ can be used as a check.

Case (b) : V/v is unknown. The calculated values $\overline{\theta}$ and $s_\theta{}^2$ are both functions of V/v and Pe. From these two equations V/v and Pe can be obtained.

To illustrate both cases, take example 2 of article : The value for $\overline{\theta}$ and $s_\theta{}^2$ are resp. :

$$\overline{\theta} = 4252/386 \text{ sec} = 11{\cdot}02 \text{ sec}$$
$$s_\theta{}^2 = 48{\cdot}07 \text{ sec}^2$$

Case (a) : $V/v = 7{\cdot}7$ sec. From Table 1, case VII

$$\overline{\vartheta} = \overline{\theta}/(V/v) = \left(1 + \frac{2}{Pe}\right) = 11{\cdot}02/7{\cdot}7 = 1{\cdot}432$$

Or $1/Pe = 0{\cdot}216$ (article 0·217)

Case (b) :

$$\frac{\overline{\vartheta}^2}{\sigma^2} = \frac{\overline{\theta}^2}{s_\theta{}^2} = \frac{(11{\cdot}02)^2}{48{\cdot}07} = \frac{(1 + 2/Pe)^2}{1/Pe^2\,(2Pe + 8)}$$

This leads to

$$1/Pe = 0{\cdot}218 \text{ (article } 0{\cdot}217)$$

and $\overline{\vartheta} = \left(1 + \frac{2}{Pe}\right) = 1{\cdot}436$ makes V/v :

$$V/v = \overline{\theta}/\overline{\vartheta} = 7{\cdot}67 \text{ sec (article } 7{\cdot}7)$$

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NOTATION

A = Cross-sectional area of tube (L^2)
C = Concentration of tracer in fluid (dimensionless)
D = Longitudinal diffusion coefficient (L^2/T)
$F = \int_0^\vartheta R d\,\vartheta$ output for a step function U (dimensionless)
L = Length of finite tube (L)
p = Parameter Laplace transformation (dimensionless)
Pe = Peclet number $u(x_\alpha - x_0)/D$ (dimensionless)
$q = \sqrt{(p/Pe + 1/4)}$ (dimensionless)
Q = Volume of tracer of unit concentration which would correspond to the actual amount of tracer introduced (L^3)
$R = CV/Q$ normalized concentration of tracer in fluid (dimensionless)
$u = v\,(x_m - x_0)/V$ average flow velocity (L/T)
$U(z)$ = Step function (dimensionless)
v = Volumetric fluid flow rate (L^3/T)
$V = A\ (x_m - x_0)$ volume of experimental section (L^3)
x = Distance from entrance of finite tube (L)
$x_\alpha - x_0$ = Length of experimental section of finite tube (L)
$z = x/(x_m - x_0)$ reduced distance from entrance of finite tube (dimensionless)
$\alpha = D_a/D$ ratio of diffusion coefficients in fore section and finite tube (dimensionless)
$\beta = D_b/D$ ratio of diffusion coefficients in after section and finite tube (dimensionless)
$\delta(\theta)$ = Dirac delta function (dimension θ^{-1})
θ = Time, measured from moment of injection (T)

$\vartheta = v\theta/V = \theta\, u/(x_m - x_0$)reduced time (dimensionless)

$\overline{\vartheta} = \int_0^\infty \vartheta\, R d\, \vartheta$ mean of the R-curve (dimensionless)

$\sigma^2 = \int_0^\infty \vartheta^2\, R d\, \vartheta - \overline{\vartheta}^2$ variance of the R curve (dimensionless)

$\overline{\theta} = \overline{\vartheta}\,(V/v)$

$s_\theta{}^2 = \sigma^2\,(V/v)^2$

Subscripts

a = Pertaining to fore section

b = Pertaining to after section

0 = The value at point of injection

m = The value at point of measurement

1 = The value at the end of the finite tube

bar over function designates the Laplace transform :

$$\overline{Q} = \int_0^\infty e^{-p\vartheta}\, Q\,(\vartheta)\, d\, \vartheta$$

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[2] Danckwerts P. V. *Chem. Engng. Sci.* 1953 **2** 1.

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Book Reviews

Plant Process Dynamic Characteristics. The Proceedings of a Conference held at Cambridge 4–6 April, 1956 by The Society of Instrument Technology. Butterworths Scientific Publications, London, 1957. xii + 246 pp. 50s.

THE President of the Society, Mr. A. J. YOUNG, remarks in the foreword to this volume that, in view of the theoretical and experimental work carried out in the last 10 years, the Control Section of the Society thought it would be profitable to hold a conference. This book is a record of 11 papers read with the discussions on each paper, the whole being welded together by a joint introduction by Drs. G. L. D'OMBRAIN and G. D. S. MACLELLAN.

In this introduction they draw attention to the advances made in the subject since IVANOFF's paper to the Institute of Fuel in 1934 and point out that there are two classes of engineers interested in the subject, i.e. process engineers who have not read or become familiar with the procedures common to servo-engineers and vice versa. They have accordingly tried to bring the two nearer together and perhaps it might be said that this was one of the chief aims of the conference. However they admit that the proceedings were weighted in the direction of chemical engineering.

Turning now to the papers which were read, one by A. HORTON, detailed experimental work on heat transfer in a jacketed pan to get information for consideration of the controllability of a plant in the design stage. R. L. DAY was concerned in a similar way with the frequency response of a distillation column reboiler in which water was boiled under natural circulation in a tube 6 ft long by 1 in. in diameter. W. L. WILKINSON and W. D. ARMSTRONG investigated the transient response in a 5 plate single bubble cap column separating benzene and carbon tetrachloride. H. VOETTER used a laboratory Oldershaw sieve tray column with sections of 9, 50 and 74 trays on *n*-heptane-benzene mixtures; he found that concentration responses could be represented by simple formulae containing residence times and the numbers of trays as the main parameters. M. W. GEERLINGS investigated the dynamic behaviour of glass electrodes for studying pH in the neutralization of either 0·05 N hydrochloric or phosphoric acid by either 5 N or 2·5 N sodium hydroxide.

G. H. THORNDIKE, R. T. D. RICHARDS and P. D. JOWETT applied control to a woollen carding machine which reduced the entanglement of fibres producing a filmy web whose thickness was controlled by absorption of a light beam on a photoelectric cell.

N. REAM, R. H. TIZARD and D. S. TOWNEND applied the N.P.L. electronic analogue computer to simulate the cascade control loop on the heavy gas oil offtake from a Kent Oil Refinery crude oil still.

J. ENDTZ, J. M. L. JANSSEN and J. C. VERMEULEN described the testing of plant units by the use of a pneumatic sine wave generator connected to a pneumatic control valve. C. A. LAWS dealt with equipment for data reduction in which processes of automatic data logging and scanning were so linked that the logging equipment only operated when deviation was detected. Finally the volume includes papers which were read by J. LEWINS and R. M. MACMILLAN and by J. H. WESTCOTT on mathematical aspects.

Enough has no doubt been said to convince all chemical engineers interested in automatic control that this is a book which they must read.

M. B. DONALD

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PAPERS APPEARING IN OTHER JOURNALS

American Institute of Chemical Engineers Journal

VOLUME 3, No. 3 SEPTEMBER, 1957

Grimm and Andersen : Move over.

Thomas J. Hanratty and James M. Engen : Interaction between a turbulent air stream and a moving water surface.

P. A. Kolodzie, Jr. and Matthew Van Winkle : Discharge coefficients through perforated plates.

James P. Hartnett and Thomas F. Irvine, Jr. : Nusselt values for estimating turbulent liquid metal heat transfer in noncircular ducts.

J. M. Lenoir and H. G. Hipkin : Equilibrium ratios of hydrogen and the critical loci of hydrogen–paraffin mixtures.

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R. C. Reid, A. B. Reynolds, A. J. Diglio, I. Spiewak and D. H. Klipstein : Two-phase pressure drops in large-diameter pipes.

Katherine S. Howard and R. A. McAllister : Surface tension of acetone–water solutions up to their normal boiling points.

Stanley Corrsin : Simple theory of an idealized turbulent mixer.

Omer Kircher and O. A. Hougen : Effect of water vapor on the catalytic oxidation of nitric oxide.

F. E. Rush, Jr. and Clifford Stirba : Measured plate efficiencies and values predicted from single-phase studies.

R. W. Ludt : Drying of sand on a hot surface.

Bernard S. Pressburg and James B. Todd : Heat transfer coefficients for condensing organic vapors of pure components and binary mixtures.

P. A. Longwell : Graphical solution of turbulent-flow diffusion equations.

H. S. Isbin, J. E. Moy and A. J. R. Da Cruz : Two-phase, steam–water critical flow.

B. D. Babcock, Glor T. Mejdell and O. A. Hougen : Catalyzed gas–liquid reactions in trickling-bed reactors.

Sakae Yagi and Daizo Kunii : Studies on effective thermal conductivities in packed beds.

S. K. Friedlander : Behavior of suspended particles in a turbulent fluid.

C. D. Holland and P. G. Murdoch : Determination of the chemical properties of an oxide catalyst in a closed system.

J. G. Stiehl and James H. Weber : Evaluation of the heat requirements in batch distillation operations.

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N. T. Hsu and B. H. Sage : Thermal and material transfer in turbulent gas streams : local transport from spheres.

D. L. Johnson, H. Saito, J. D. Polejes and O. A. Hougen : Effects of bubbling and stirring on mass transfer coefficients in liquids.

J. A. Consiglio and C. M. Sliepcevich : Effect of liquid physical properties and flow rates on the surface area of sprays from a pressure atomizer.

George Thodos : Critical constants of the aromatic hydrocarbons.

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J. Fafchamps : Recherches sur l'enthalpie moyenne d'un écoulement gazeux. *Revue Universelle des Mines, Liége* 1957 **13** No. 1, 3.

La détermination de l'enthalpie moyenne d'un écoulement gazeux comporte deux mesures, celle du débit en poids et celle de la température moyenne. Une définition rigoureuse de la température moyenne fait ressortir la nécessité d'une étude théorique et expérimentale des champs de vitesse et de température.

Insuffisance d'une mesure unique au moyen des sondes classiques. Utilité d'un dispositif stabilisateur de l'écoulement : son efficacité. Étude expérimentale du positionnement des sondes dans les écoulements symétriques et modérément dissymétriques. Confrontation des résultats avec les lois généralement admises dans les problèmes d'écoulement et de transmission de chaleur en conduite.

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Equation (22) in top right-hand column of p. 186 should read :

$$\tau = \left(\tau_{m0} + \frac{10}{3}\right) \exp\left(\frac{\alpha\theta}{2}\right) - \frac{10}{3}.$$

Equation (33) on p. 188 should read as follows :

As indicated in equation (5) :

$$\gamma = \frac{\int_A f(\rho)\, dA}{A}.$$

For case II

$$\tau = \tau_m f(\rho) + C$$

where $f(\rho) = 1 - 3\rho^2 + 2\rho^3$

$$C = z(\rho^2 - \rho^3)$$

Thus $\gamma = 0{\cdot}3$

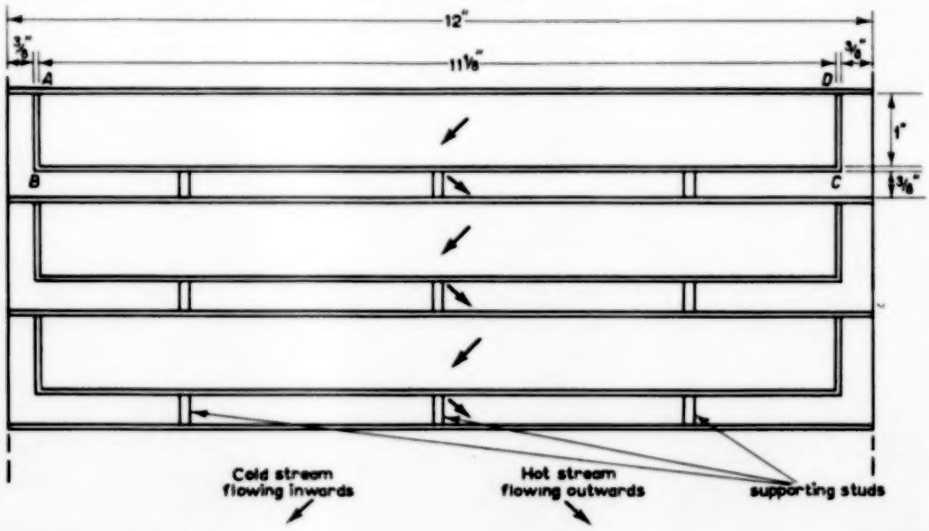
$$\lambda = 2z/\tau_m$$

HAMMER, EGIL and LYDERSEN A. L., The vapour pressure of di-*n*-butylphthalate, di-*n*-butylsebacate, lauric acid and myristic acid. *Chem. Engng. Sci.* 1957 **7** 66.

On p. 69 Figs. 1 and 2 should be transposed.

BAIRD M. H. I., MCGRAE W., RUMFORD F. and SLESSER C. G. M., Some considerations on heat transfer in spiral plate-heat exchangers. *Chem. Engng. Sci.* 1957 **7** 112.

Fig. 1, p. 112 should be marked *A*, *B*, *C* and *D*, as in the revised figure below.



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